

UNCLASSIFIED

AD NUMBER	
AD368613	
CLASSIFICATION CHANGES	
TO:	UNCLASSIFIED
FROM:	CONFIDENTIAL
LIMITATION CHANGES	
TO: Approved for public release; distribution is unlimited.	
FROM: Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; SEP 1965. Other requests shall be referred to Office of Naval Research, Washington, DC.	
AUTHORITY	
per ONR ltr 4 May 1977 per ONR ltr 4 May 1977	

THIS PAGE IS UNCLASSIFIED

THIS REPORT HAS BEEN DELIMITED
AND CLEARED FOR PUBLIC RELEASE
UNDER DOD DIRECTIVE 5200.20 AND
NO RESTRICTIONS ARE IMPOSED UPON
ITS USE AND DISCLOSURE.

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

SECURITY

MARKING

The classified or limited status of this report applies to each page, unless otherwise marked.

Separate page printouts MUST be marked accordingly.

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C., SECTIONS 793 AND 794. THE TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

CONFIDENTIAL

Report RMD 5043-Q3-65

Contract No. NOnr 4364(00)

368613

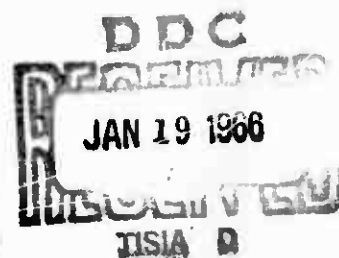
(U)

ADVANCED OXIDIZER RESEARCH

Report Period: 1 July 1965 to 30 September 1965

Research reported in this publication was supported
by the Advanced Research Projects Agency.

GROUP 4
DOWNGRADED AT 3-YEAR INTERVALS;
DECLASSIFIED AFTER 12 YEARS



Thiokol

CHEMICAL CORPORATION

REACTION MOTORS DIVISION

DENVILLE, NEW JERSEY

CONFIDENTIAL

"This document contains information affecting the National defense of the United States within the meaning of the Espionage Laws, Title 18, U. S. C., Sections 793 and 794. Its transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law."

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

(U)

ADVANCED OXIDIZER RESEARCH

Report RMD 5043-Q3-65

Report Period: 1 July 1965 to 30 September 1965

Report Date: 30 September 1965

Contract No. NONr 4364(00), ARPA Order No. 417, Amendment No. 2

Submitted by:

Donald D. Ferry
DONALD D. FERRY
Supervisor, Synthetic
Chemical Research Section

Approved by:

Murray S. Cohen
MURRAY S. COHEN
Manager, Chemistry
Department

David J. Mann
DAVID J. MANN
Director of Research

CONFIDENTIAL

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

PREVIOUS PAGE WAS BLANK, THEREFORE NOT FILMED.

GENERAL FOREWORD

This quarterly report was prepared by the Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, and summarizes work in the area of advanced oxidizer chemistry being conducted at this Division under the sponsorship of the Advanced Research Projects Agency. The work was administered by the Department of Navy, Office of Naval Research, with Mr. R. L. Hanson serving as Scientific Officer.

This report consists of the three following sections:

<u>Section</u>	<u>Task No.</u>	<u>Title</u>
I	51	Organic Difluoramine Chemistry
II	53	Inorganic Oxidizer Synthesis
III	55	Thermal Stability of Advanced Solid Oxidizers

— iii —

CONFIDENTIAL

Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

ABSTRACT

This report describes research conducted at Thiokol Chemical Corporation, Reaction Motors Division, directed toward the development of advanced solid oxidizers. The three major tasks on which work has been performed are listed below, together with an abstract of each task, and are included as three separate sections of this report.

SECTION I - ORGANIC DIFLUORAMINE CHEMISTRY

Further experiments on the dehydrofluorination of secondary alkyldifluoramines are described. A new partially dehydrofluorinated product, 1-difluoramino-2-fluoriminocyclohexane, has been obtained by treating bis-(difluoramino)cyclohexane with basic ion exchange resin for a limited time.

Bis(difluoramino)fluoraminomethoxypentane was synthesized by the addition of pentanol to perfluoroguanidine. The adduct was stable to vacuum distillation but lost the elements of HNF_2 to yield N, N, N'-trifluoropentoxiformamidine upon exposure to a Halocarbon chromatographic column.

1, 1-Bis(difluoramino)phenylethane and 1, 1-bis(difluoramino)heptane were synthesized in sufficiently high purity for thermal sensitivity and heat of formation determinations, respectively.

SECTION II - INORGANIC OXIDIZER SYNTHESIS

Elemental analyses of the $\text{N}_2\text{F}_4\text{-AsF}_5$ adduct give a composition, $\text{N}_2\text{F}_4(\text{AsF}_5)_{1.33}$, indicating a mixture of adducts having 1:1 and 1:2 $\text{N}_2\text{F}_4\text{:AsF}_5$ ratios. Evidence presented previously that the adduct is ionic and contains the N_2F_3^+ cation still appears valid. The structure of the 1:2 adduct is possibly $\text{N}_2\text{F}_3^+\text{As}_2\text{F}_{11}^-$.

The reaction of N_2F_4 with HAsF_6 gives a solid N-F compound having X-ray and infrared spectra different from $\text{N}_2\text{F}_3\text{AsF}_6$. No reaction occurred when N_2F_4 was treated with HClO_4 in HF. Unsuccessful attempts were made to prepare $\text{N}_2\text{F}_3\text{ClO}_4$ by reacting $\text{N}_2\text{F}_3\text{AsF}_6$ with metal perchlorates in HF.

CONFIDENTIAL

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

The reaction of O_2AsF_6 with CsClF_4 produces O_2 and Cl_2 , as well as CsAsF_6 , at about 0°C . The reaction of NO_2 with AsF_5 does not give a molecular adduct $\text{NO}_2 \cdot \text{AsF}_5$ as reported in the literature, but rather a mixture of NOAsF_6 and NO_2AsF_6 .

SECTION III - THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

The presence of ammonium perchlorate as a decomposition product of hydroxylammonium perchlorate was found to be dependent on the removal of oxidizing species from the system and, hence, non-stoichiometric. The oxidation of ammonium perchlorate by anhydrous perchloric acid at elevated temperatures was demonstrated.

— v —

CONFIDENTIAL

Report RMD 5043-Q3-65

SECTION I

TASK 51

ORGANIC DIFLUORAMINE CHEMISTRY

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

Section I

ORGANIC DIFLUORAMINE CHEMISTRY

Harry F. Smith
Joseph J. Dvorak

Report RMD 5043-Q3-65

RMD Project 5043, Task 51
Report Period: 1 July 1965
to 30 September 1965

Contract No. NONr 4364(00)
ARPA Order No. 417
Project Code 5910

CONFIDENTIAL

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

PREVIOUS PAGE WAS BLANK, THEREFORE NOT FILMED.

FOREWORD

This section of the quarterly progress report on advanced oxidizers describes research performed from 1 July 1965 to 30 September 1965 on the synthesis and chemical reactions of organic fluoronitrogen compounds, and on the preparation of selected difluoramino compounds for structure-sensitivity correlation studies.

Technical personnel contributing to this effort were: H. F. Smith (Project Supervisor), J. J. Dvorak, W. H. Wieting, and P. Shapiro (Synthesis). Analytical support was provided by D. G. Chowanec, J. A. Creatura, D. F. Kates, and D. N. Pregler.

— iii —

CONFIDENTIAL

Task 51
Report RMD 5043-Q3-6

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

ABSTRACT

Further experiments on the dehydrofluorination of secondary alkyldifluoramines are described. A new partially dehydrofluorinated product, 1-difluoramino-2-fluoriminocyclohexane, has been obtained by treating bis(difluoramino)cyclohexane with basic ion exchange resin for a limited time.

Bis(difluoramino)fluoraminomethoxypentane was synthesized by the addition of pentanol to perfluoroguanidine. The adduct was stable to vacuum distillation but lost the elements of HNF_2 to yield N, N, N'-trifluoropentoxoformamidine upon exposure to a Halocarbon chromatographic column.

1, 1-Bis(difluoramino)phenylethane and 1, 1-bis(difluoramino)heptane were synthesized in sufficiently high purity for thermal sensitivity and heat of formation determinations, respectively.

CONFIDENTIAL

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

CONTENTS

	Page
I. INTRODUCTION	1
II. DISCUSSION	3
A. Dehydrofluorination Reactions	3
B. Addition Reactions of Activated Fluorimines	8
C. Chemistry of Bis(difluoramino)fluoraminomethoxy- alkanes	9
D. Synthesis and Purification of 1,1-Bis(difluoramino)- phenylethane	16
E. Purification of 1,2-Bis(difluoramino)ethane	18
F. Synthesis and Purification of 1,1-Bis(difluoramino)- heptane	18
III. EXPERIMENTAL	22
A. 1-Difluoramino-2-fluoriminocyclohexane	22
B. Attempted Reaction of N,N,N'-Trifluorobenzamidine with n-Butanol	22
C. Bis(difluoramino)fluoraminomethoxypentane	22
D. 1,1-Bis(difluoramino)phenylethane	23
E. 1,1-Bis(difluoramino)heptane	23
IV. FUTURE WORK	24
V. REFERENCES	25

— v —
CONFIDENTIAL

Task 51
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

ILLUSTRATIONS

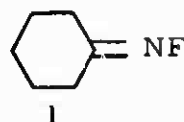
Figure		Page
1.	Infrared Spectrum of Partially Dehydrofluorinated 1,2-Bis(difluoramino)cyclohexane	5
2.	Infrared Spectrum of 1,2-Bis(difluoramino)cyclohexane	6
3.	Infrared Spectrum of 1,2-Difluoriminocyclohexane	7
4.	Infrared Spectrum of Crude Pentanol Adduct of Perfluoroguanidine	11
5.	V.P.C. of Crude Pentanol Adduct of Perfluoroguanidine	12
6.	Repass V.P.C. of Fraction Under Peak B	13
7.	Infrared Spectrum of Fraction Under Peak B	14
8.	Repass V.P.C. of Fraction Under Peak C	15
9.	Infrared Spectrum of N, N, N'-Trifluoropentoxoformamidine	17
10.	Infrared Spectrum of 1,1-Bis(difluoramino)phenylethane	19
11.	V.P.C. of 1,1-Bis(difluoramino)ethane After 22 Months Storage	20
12.	V.P.C. of Chromatographed 1,1-Bis(difluoramino)ethane	21

CONFIDENTIAL

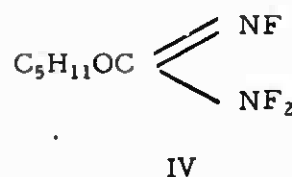
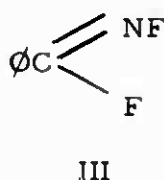
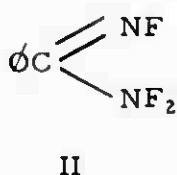
I. INTRODUCTION

The research described in this report has been directed toward the same two objectives that guided our earlier work. Our primary objective has been to elucidate some of the chemistry of organic fluoronitrogen compounds pertaining to the field of high-energy propellant oxidizers. A smaller effort is directed toward the synthesis of certain difluoramino compounds for studies seeking to correlate thermal sensitivity with structure.

The immediate area of interest of the exploratory portion of our program is an investigation of the chemical reactions of compounds containing the keto-fluorimino group, $>C=NF$. Some effort was devoted to the synthesis of one of the simplest of such model compounds, cyclohexylidenefluorimine (I), and to studying the intricacies of the dehydrofluorination of other difluoramines. Several new model compounds containing substituents of high electronegativity



(II, III, IV) have been synthesized and an exploration of their addition



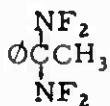
reactions has begun. These models are electronically analogous to per-fluoroguanidine, and it is anticipated that some of the same kinds of reaction will occur.

Two new compounds have been synthesized in high purity for physico-chemical studies in other laboratories. These are 1,1-bis(difluoramino)-phenylethane (V) for sensitivity evaluation at the Naval Ordnance Laboratory

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

and 1,1-bis(difluoramino)heptane (VI) for heat-of-formation determination at the Bureau of Mines. In addition, an old sample of 1, 2-bis(difluoramino)



V



VI

ethane was repurified for sensitivity studies.

CONFIDENTIAL

CONFIDENTIAL

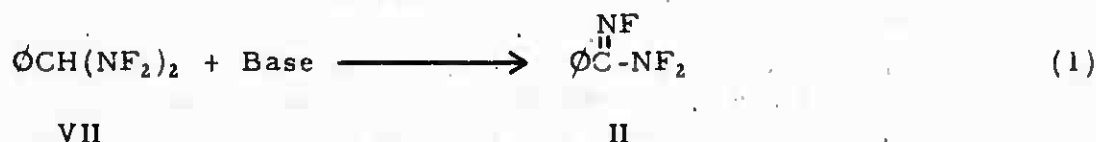
Thiokol
REACTION MOTORS DIVISION

II. DISCUSSION

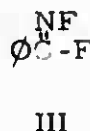
A. DEHYDROFLUORINATION REACTIONS

The dehydrofluorination of three compounds, cyclohexyldifluoramino, 1,2-bis(difluoramino)cyclohexane and α,α -bis(difluoramino)toluene, was conducted in order to obtain appropriate fluorimino model compounds which could be used in elucidating the chemistry of the ketofluorimino group, $>C=NF$.

Dehydrofluorination of α,α -bis(difluoramino)toluene (VII), as previously reported (Ref 1), again resulted in a two-component mixture which contained the desired N,N,N'-trifluorobenzamidine (Equation 1). On the basis



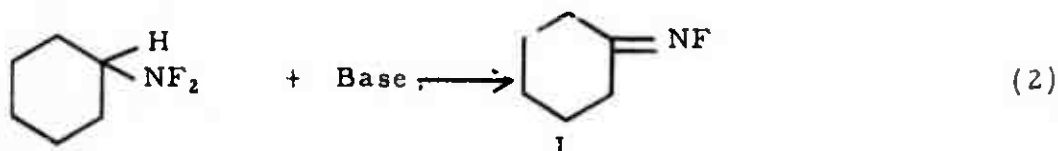
of infrared spectral data, the second component has been tentatively assigned the structure III. Unfortunately, sufficient material for an unequivocal char-



acterization of this second component has not been obtained.

Some difficulties have been encountered in the dehydrofluorination of cyclohexyldifluoramino (Equation 2). In several instances, the distillation of

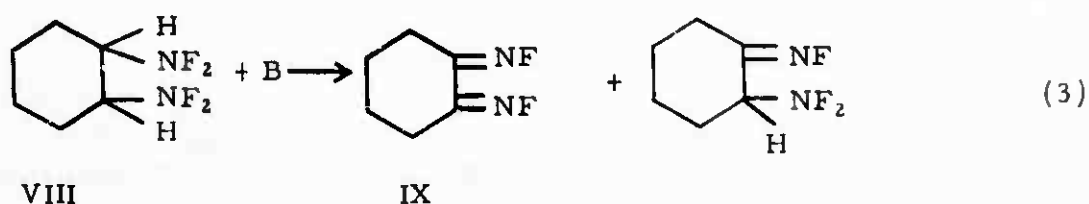
CONFIDENTIAL



the crude product, obtained by treating the cyclohexyldifluoramino with basic ion exchange resin, was accompanied by decomposition. Surprisingly, decomposition appeared to occur in the condenser. Any liquid returning to the pot from the distillation column remained colorless. As yet, we can offer no explanation for this observation.

In one experiment, decomposition was observed as soon as the cyclohexyldifluoramino was added to an ether suspension of the resin. In this instance, however, the batch of resin used was different from that used for the previous successful dehydrofluorination of VII. Presumably, some contaminant in the resin, such as water, contributed to the decomposition.

A very interesting result was obtained in one experiment in which the time for reaction between 1,2-bis(difluoramino)cyclohexane (VIII) and Amberlite IR-45 resin was cut short. Normally, the difluoramino compound subjected to dehydrofluorination is allowed to react with the resin for approximately 20 hr. In this instance, however, after 6 hr. the resin appeared to be consumed and the reaction was quenched by filtering the mixture. Distillation of the crude reaction product gave three fractions. The first and predominant fraction consisted of unreacted 1,2-bis(difluoramino)cyclohexane (VIII). The third fraction consisted of 1,2-difluoriminocyclohexane (IX). The infrared spectrum of the second fraction, however, indicates the presence of both fluoramino ($-\text{NF}_2$) and fluorimino ($=\text{NF}$) groups, possibly in the same molecule (Figure 1). Infrared curves of VIII and IX are shown for reference in Figures 2 and 3, respectively. These results suggest that dehydrofluorination of a difluoramino group



B = Amberlite IR-45 resin

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

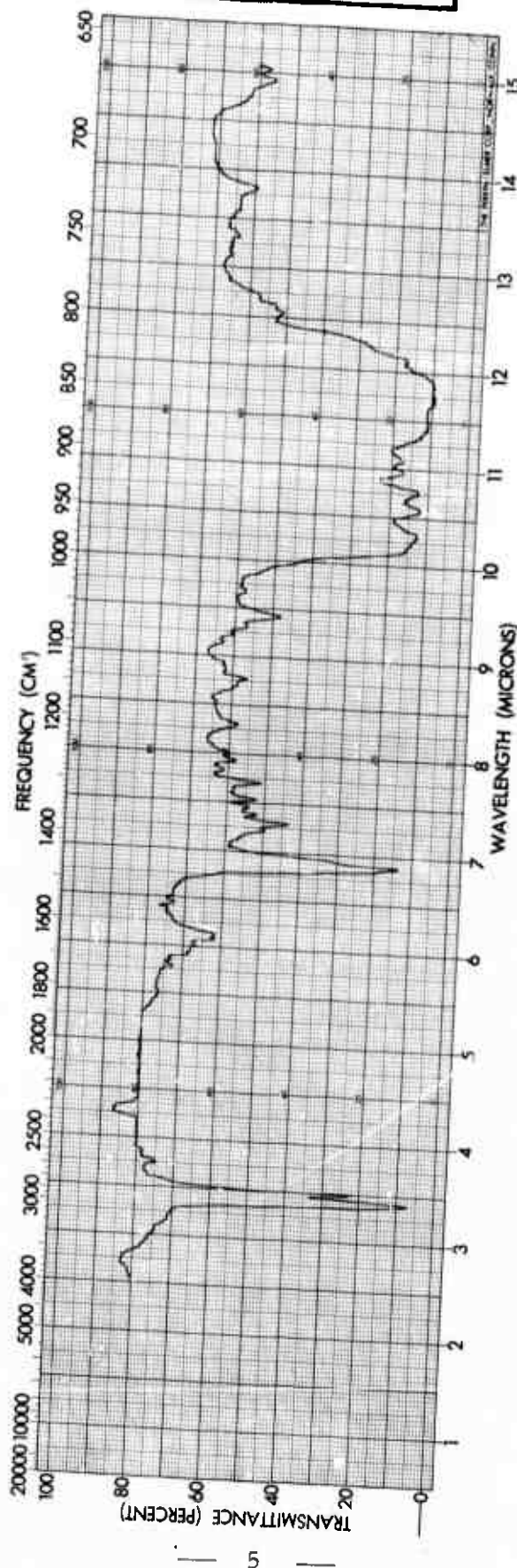


Figure 1. Infrared Spectrum of Partially Dehydrofluorinated 1,2-Bis(difluoramino)cyclohexane

CONFIDENTIAL

Task 51
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

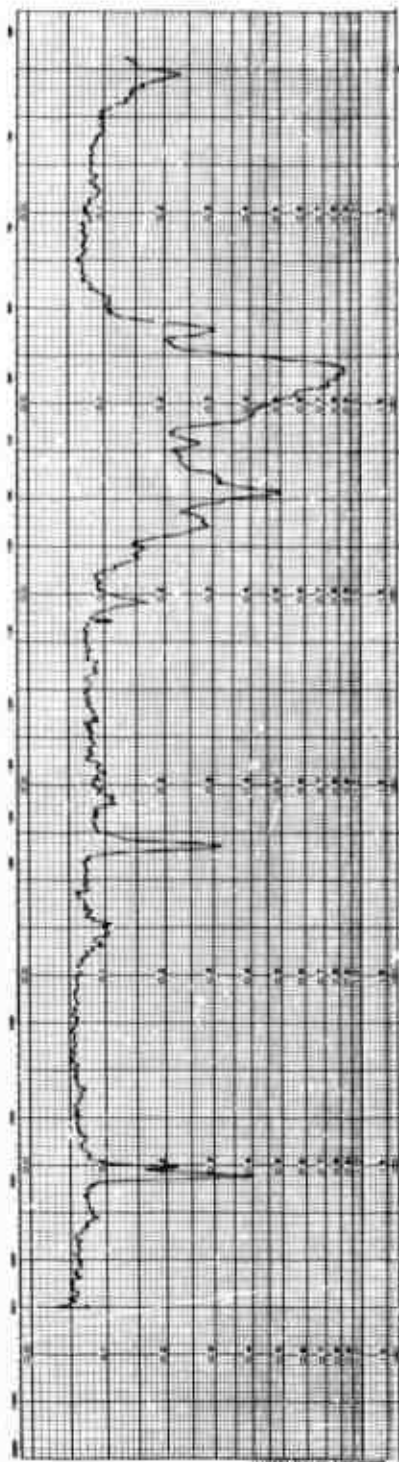


Figure 2. Infrared Spectrum of 1,2-Bis(difluoramino)cyclohexane

— 6 —

CONFIDENTIAL

Task 51
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

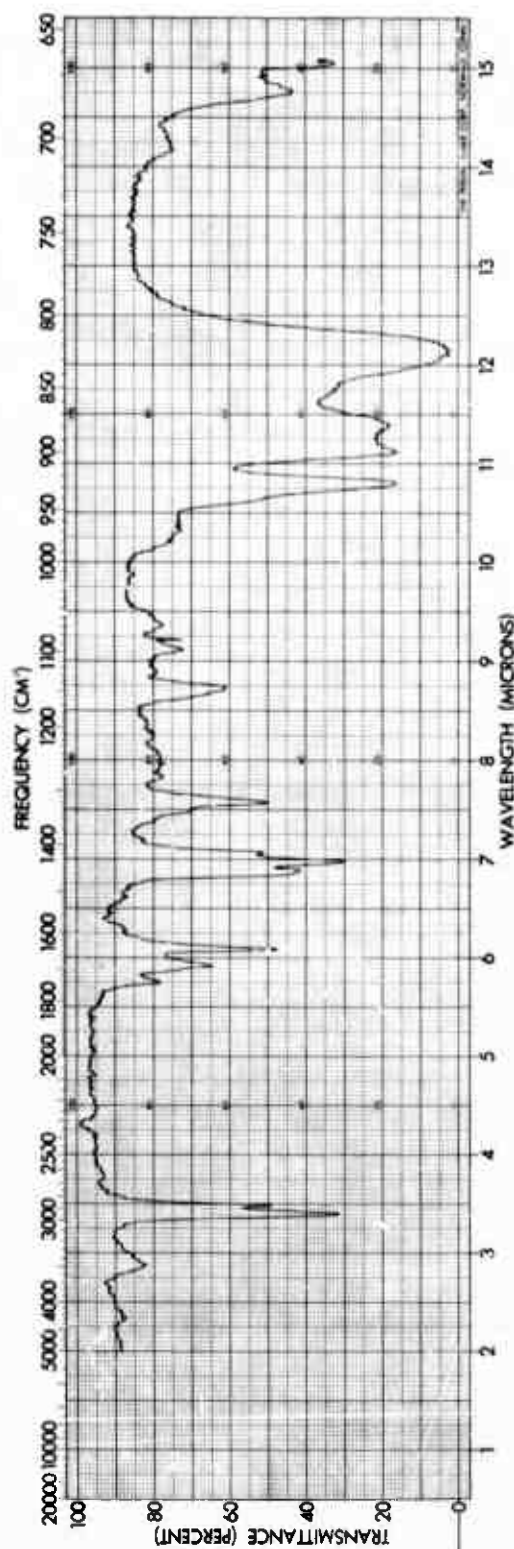


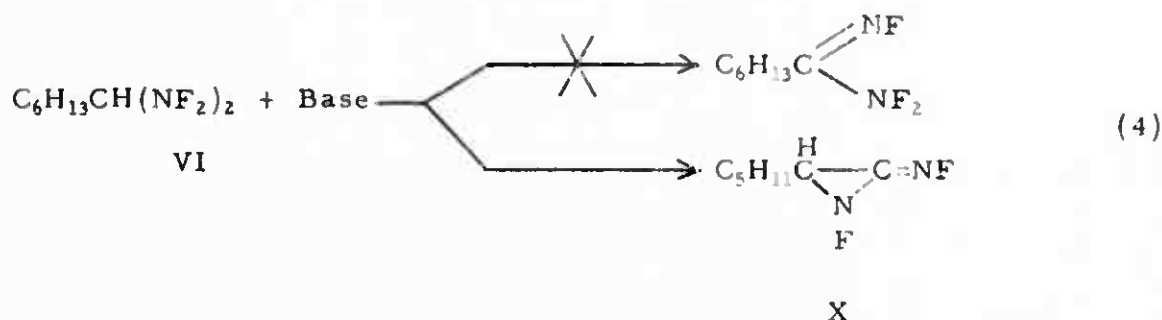
Figure 3. Infrared Spectrum of 1,2-Difluorinocyclohexane

— 7 —

CONFIDENTIAL

Task 51
Report RMD 5043-Q3-65

in a position vicinal to a fluorimino group proceeds somewhat more rapidly than the initial dehydrofluorination producing the first fluorimino group. It is problematical whether this observation has any bearing on the dehydrofluorination of gem-bis(difluoramines) to trifluoroamidines. The elimination of a second equivalent of hydrogen fluoride, in the reaction of 1,1-bis(difluor-amino)heptane (VI) for example (Ref 2), gave a product of probable structure



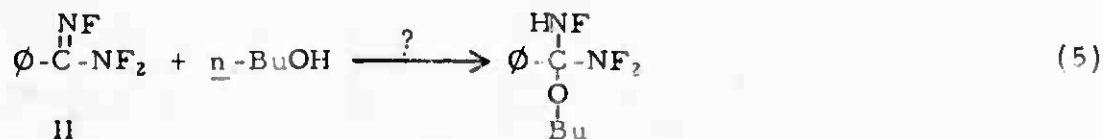
X, rather than the desired amidine. In future dehydrofluorination experiments, the effect of introducing the base into an excess of the difluoramine will be examined.

In one experiment, VIII was treated with ethyldiisopropylamine in place of the ion exchange resin. Subsequently, the reaction mixture was washed with water and the organic layer was separated and dried. After the solvent was evaporated at room temperature, the crude yellow oil spontaneously darkened and rapidly decomposed. The cause of this decomposition is unknown.

B. ADDITION REACTIONS OF ACTIVATED FLUORIMINES

In order to define the nature and scope of reactions involving the keto-fluorimine group, >C=NF , an investigation of the chemical reactions of new model compounds containing electronegative substituents has been initiated. Of these model compounds, N,N,N'-trifluorobenzamidine (II) was selected for intensive study.

Since perfluoroguanidine is known to undergo addition reactions with alcohols, an investigation of the reaction of II with n-butanol (Equation 5)



CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

was started in order to determine those factors which influence the course and extent of reaction and the physical and chemical stability of the products.

In a preliminary experiment, II was added to a mixture of n-butanol and urea in Freon-113. The reaction mixture was stirred for several hours at 0°C and then overnight at ambient temperature. Under these conditions no reaction was found to occur. In future experiments, the effects of heat, pressure and a variety of catalysts will be explored.

C. CHEMISTRY OF BIS(DIFLUORAMINO)FLUORAMINOMETHOXYALKANES

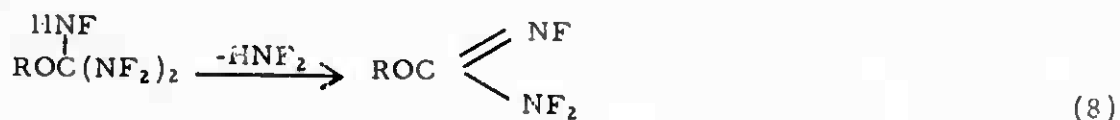
A route to one of the most energetic classes of difluoramino compounds involves the addition of alcohols to perfluoroguanidine (Equation 6)



and the subsequent fluorination of the fluoramino intermediate (Equation 7). The



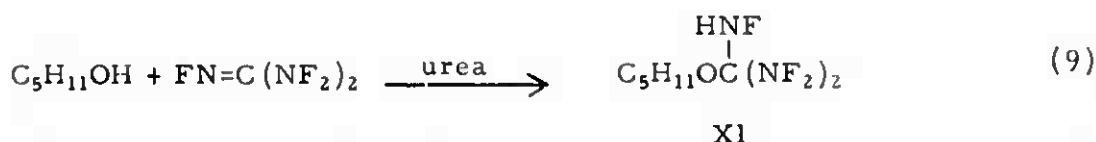
relative instability of the intermediate, which tends to eliminate the elements of HNF_2 to form an alkoxyformamidine (Equation 8), has been a major source of difficulty



and has impeded the successful utilization of this system (Ref 3). We have undertaken an investigation of the conditions which favor this decomposition reaction in order to provide information which will be valuable in avoiding it. At the same time, we will be producing a compound containing an electro-negatively activated fluorimino group, which will be useful in reaction studies aimed at defining the scope and limitations of addition reactions.

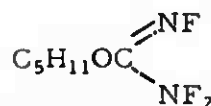
CONFIDENTIAL

An adduct (XI) was prepared from pentanol and perfluoroguanidine (Equation 9)



using previously established procedures (Ref 3). The crude product was shown by its infrared absorption curve (Figure 4) to be principally XI. An N-H peak was observed at about 3150 cm^{-1} along with N-F absorptions in the $850\text{-}1000 \text{ cm}^{-1}$ region, but there was no indication of C=N at 1800 cm^{-1} . When this material was chromatographed on a Halocarbon oil column, it appeared to contain three major components (Figure 5). Fractional distillation under vacuum gave no clearly defined boiling point plateaus. Three distillation fractions were separated, and each exhibited a three-peak v.p.c. trace similar to that of the crude mixture. When the fraction represented by peak B was collected and repassed through the v.p.c. column, it gave a major peak at essentially the same retention time, accompanied by a small peak corresponding to peak A (Figure 6). The infrared spectrum of this fraction (Figure 7) contained the expected absorptions for IV (C=N at 1800 cm^{-1} , no N-H at 3150 cm^{-1}) plus smaller peaks due to water and acetone which apparently condensed with the fraction during its collection. Upon rechromatographing material collected from peak C, we obtained a trace containing a prominent peak corresponding to B and a very small residual peak at C (Figure 8).

From these observations, we conclude that the adduct XI was the principal product



IV

formed in the reaction, and that this compound was stable to distillation under vacuum. Passing through the Halocarbon oil v.p.c. column caused the decomposition of XI (peak C) leading to IV (peak B). The identity of the compound which produced peak A in the chromatogram of the crude reaction product has not been determined.

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

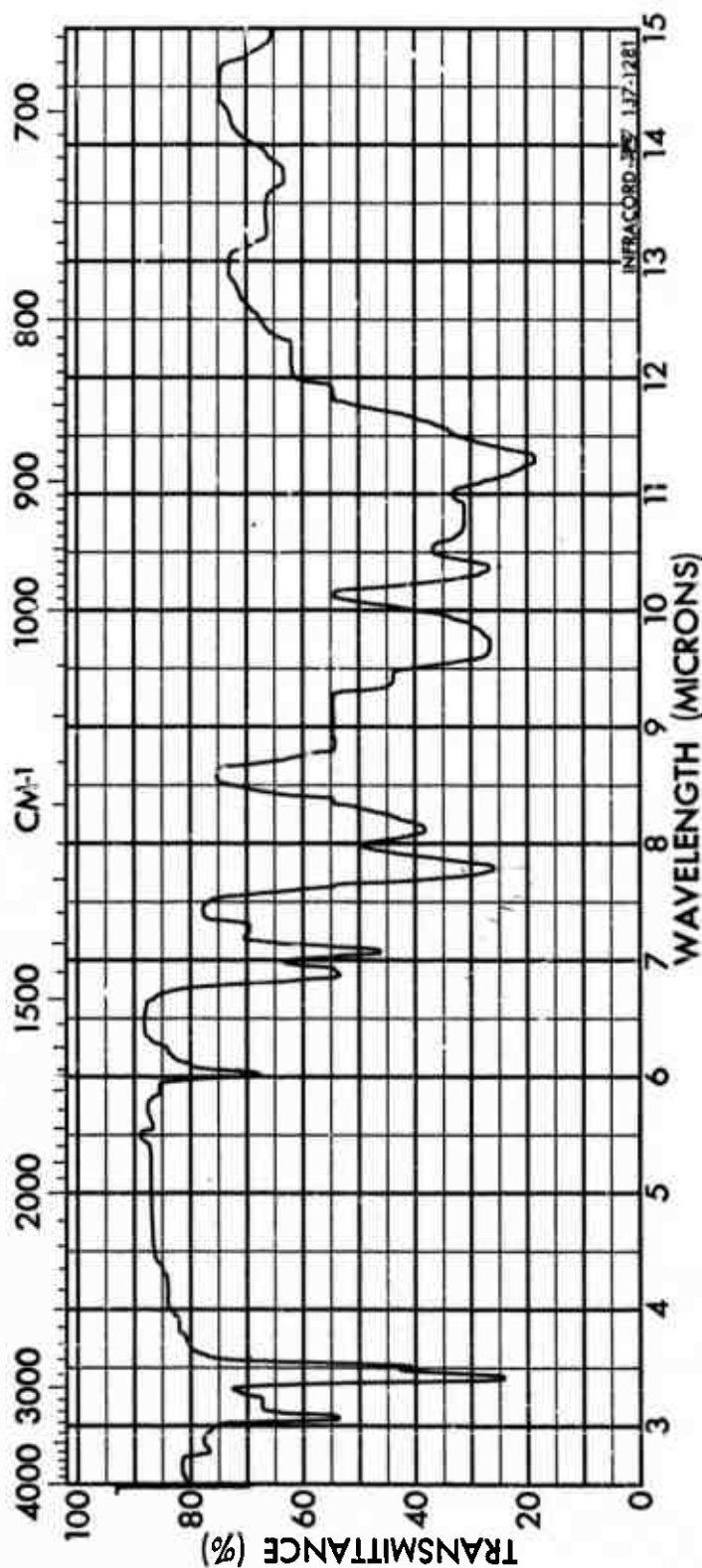


Figure 4. Infrared Spectrum of Crude Pentanol Adduct of Perfluoroguanidine

CONFIDENTIAL

Task 51
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

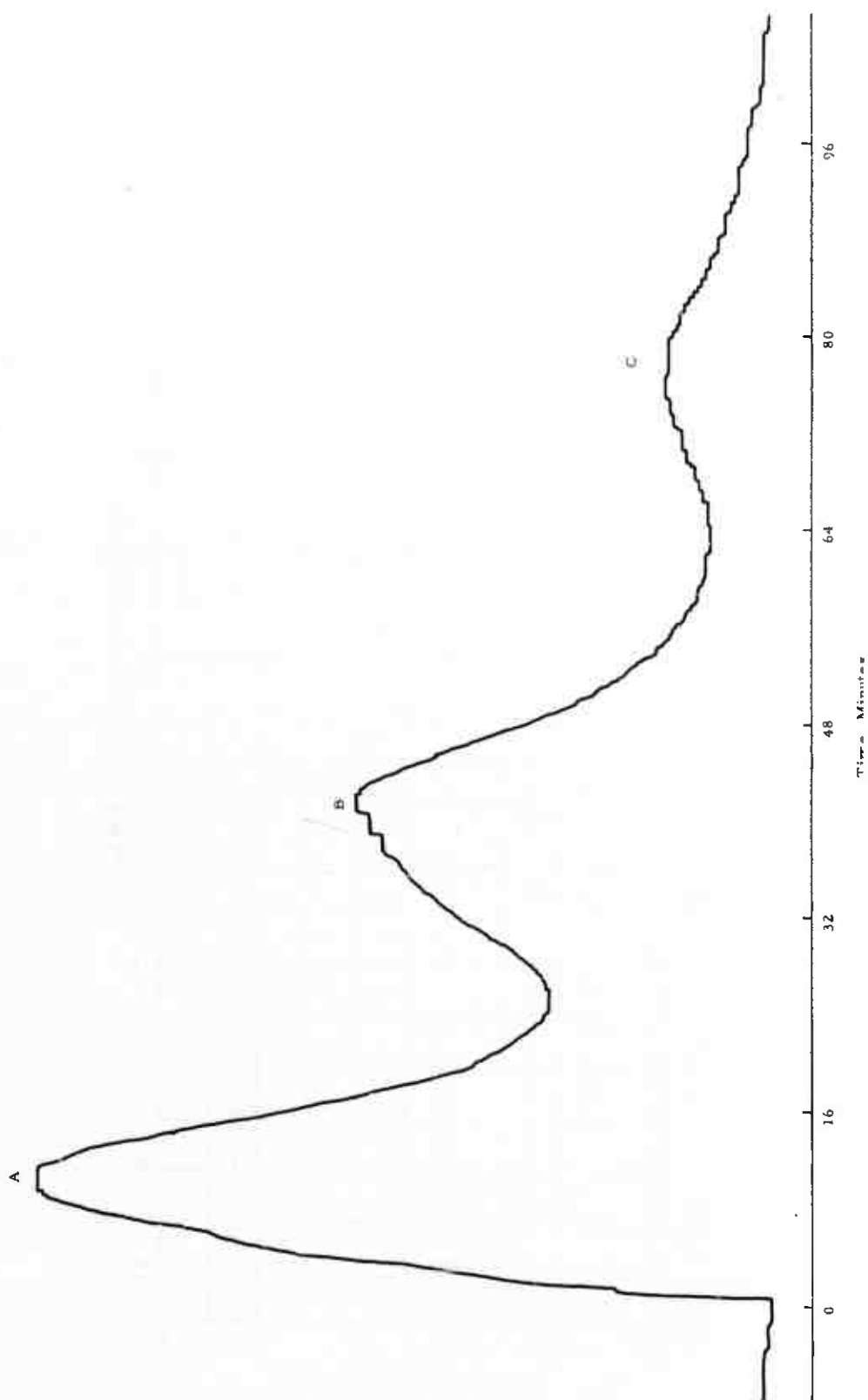


Figure 5. V.P.C. of Crude Pentanol Adduct of Perfluoroguanidine

CONFIDENTIAL

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

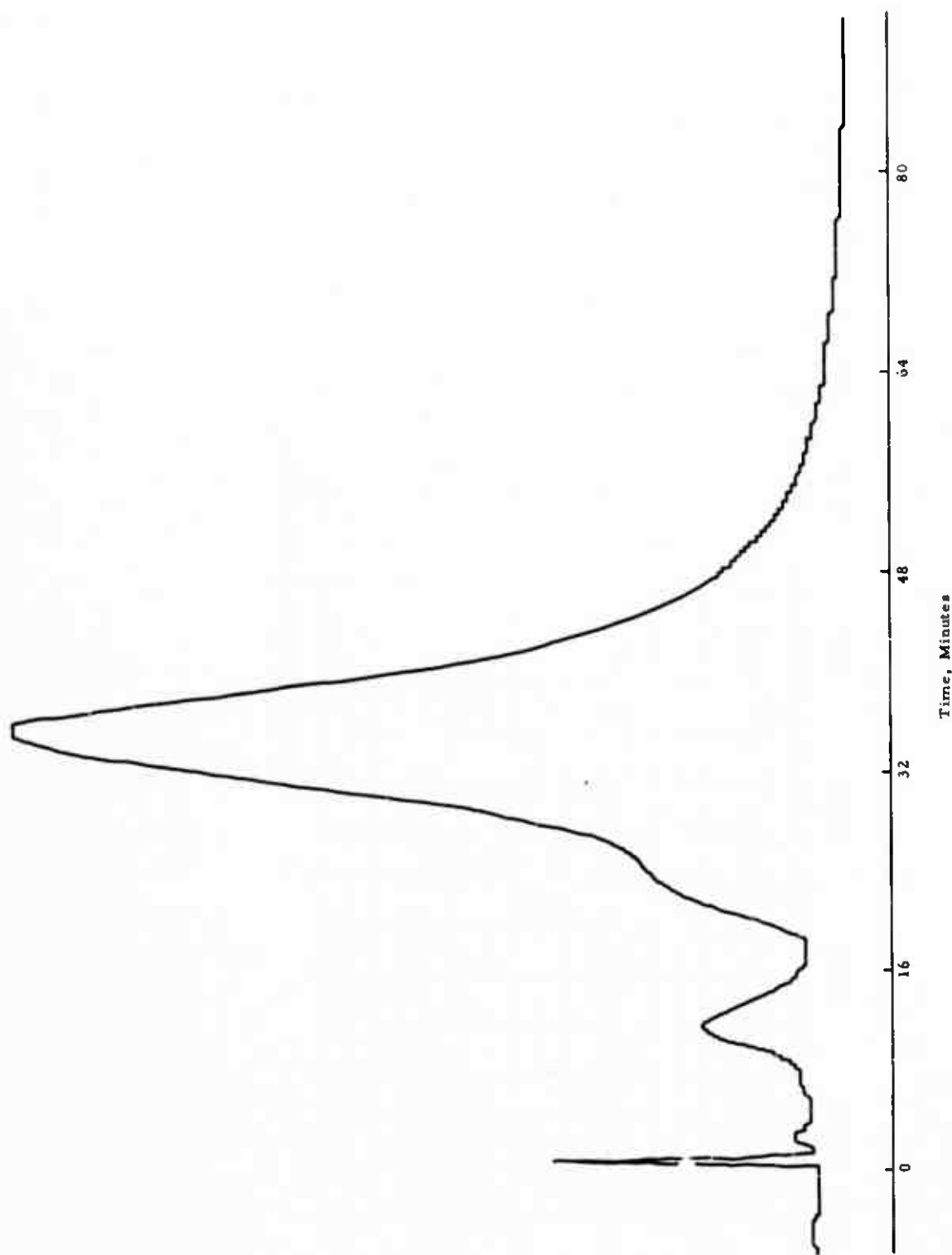


Figure 6. Repass V.P.C. of Fraction Under Peak B

— 13 —

CONFIDENTIAL

Task 51
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

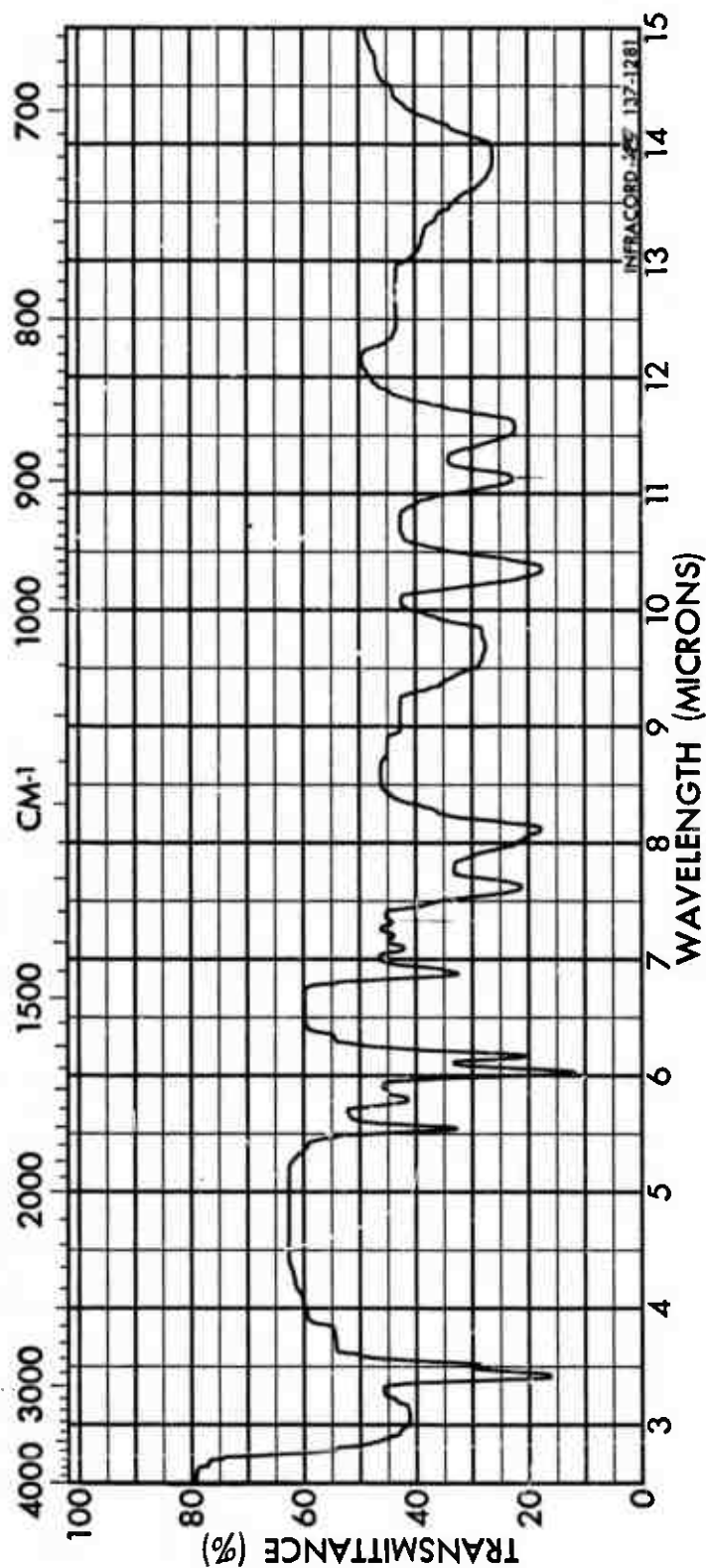


Figure 7. Infrared Spectrum of Fraction Under Peak B

— 14 —

CONFIDENTIAL

Task 51
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

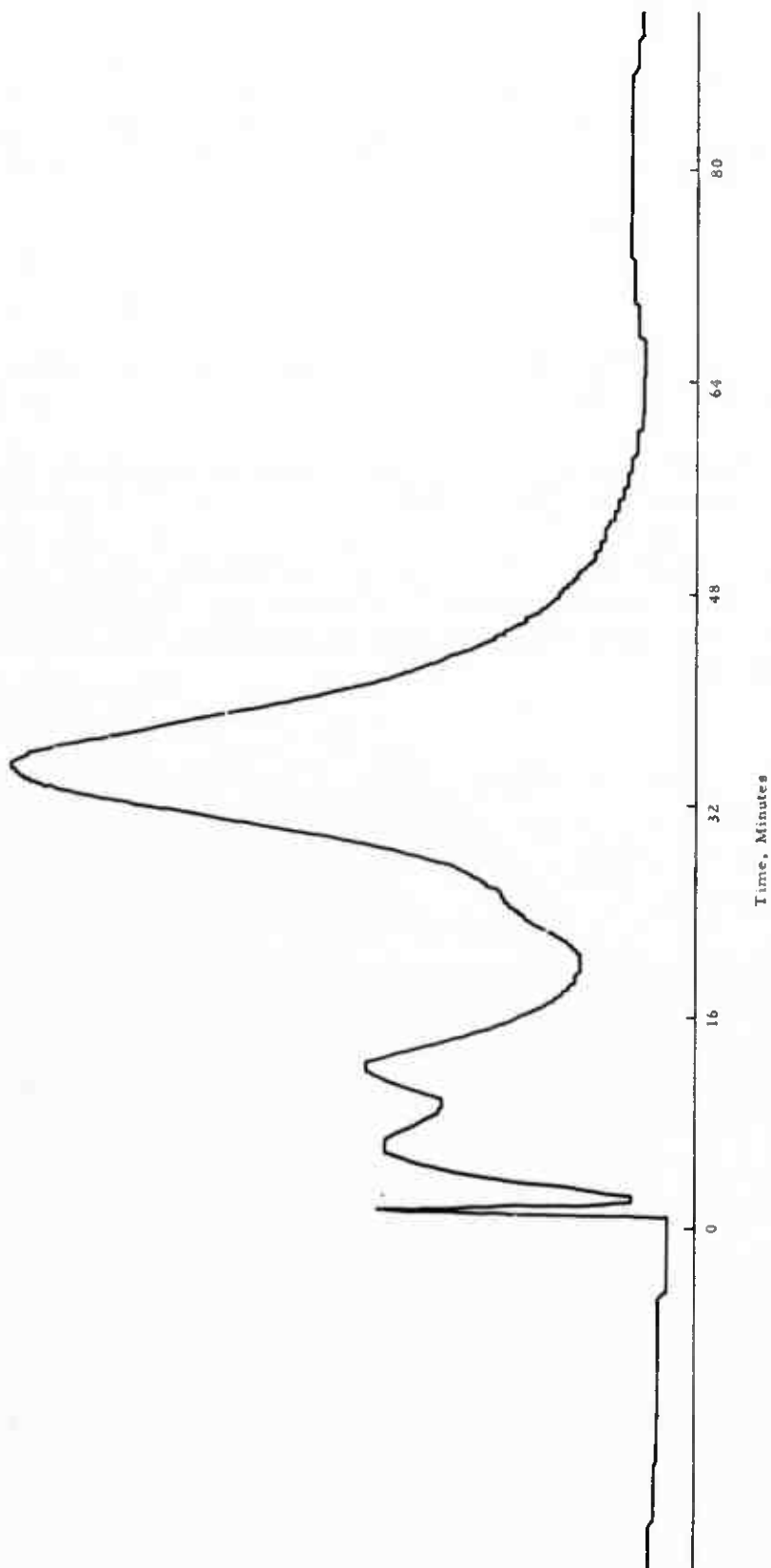


Figure 8. Repass V.P.C. of Fraction Under Peak C

— 15 —

CONFIDENTIAL

Task 51
Report RMD 5043-Q3-65

CONFIDENTIAL

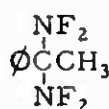
Thiokol
REACTION MOTORS DIVISION

A portion of the material collected under peak B was purified by an additional v. p. c. pass to provide a sample for characterization. The results of infrared (Figure 9) and elemental analyses were completely in accord with the assigned structure IV.

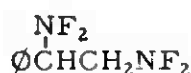
Anal. calcd. for $C_6H_{11}N_2F_3O$: C, 39.13; H, 6.02; N, 15.21
Found: C, 40.64; H, 6.32; N, 14.47

D. SYNTHESIS AND PURIFICATION OF 1,1-BIS(DIFLUORAMINO)-
PHENYLETHANE

The sensitivity of various difluoramino compounds to thermal shock is being measured at the Naval Ordnance Laboratory, Silver Spring, Md., in an effort to correlate such sensitivity with a variety of structural features. As a part of this program, we have undertaken to supply samples of a series of isomeric aromatic difluoramino compounds. This series consists of 1,1-, 1,2-, and 2,2-bis(difluoramino)phenylethane (XII, XIII, and XIV, respectively).



XII

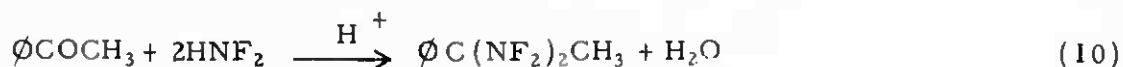


XIII



XIV

The preparation and purification of the vicinal disubstituted compound (XIII) has been described in an earlier report (Ref 4) and some aspects of the synthesis of XIV have also been discussed (Ref 1). The synthesis of XII was accomplished by the reaction of difluoramine with acetophenone (Equation 10) in the usual manner.



XII

Purification was complicated by the fact that XII could not be separated from acetophenone either by vacuum distillation or by v. p. c. on a variety of stationary phases. Purification to a satisfactory level (99%) was accomplished by extracting a Freon-113 solution of the crude product with concentrated sulfuric acid. Distillation of the washed material gave a product free

CONFIDENTIAL

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

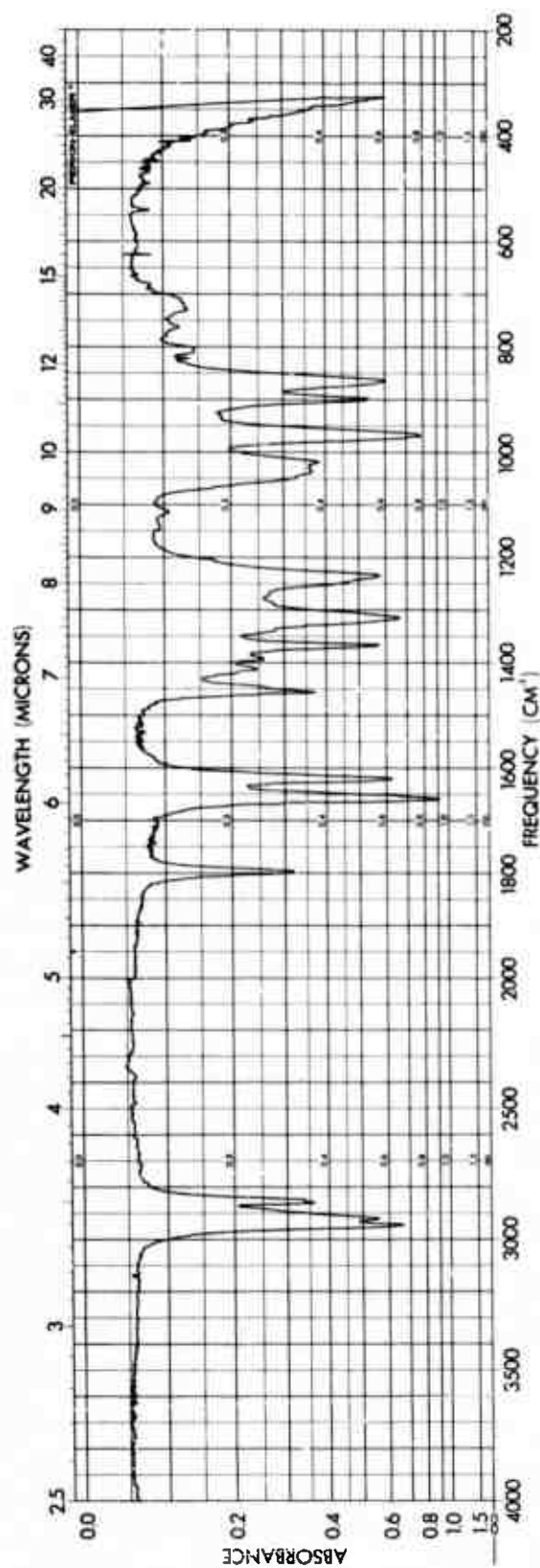


Figure 9. Infrared Spectrum of N, N, N'-Trifluoropentoxymethanamine

CONFIDENTIAL

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

of carbonyl contaminants, as indicated by its infrared spectrum (Figure 10).

E. PURIFICATION OF 1,2-BIS(DIFLUORAMINO)ETHANE

The title compound became of interest again for thermal sensitivity studies at NOL. A sample of this material, which had been in storage at 0° for 22 months, was reexamined and found to contain an impressive array of contaminants. The v.p.c. trace is reproduced in Figure 11. Since v.p.c. equipment was not available at the time the compound was originally synthesized (Ref 4), no direct comparison with the fresh material is possible. Elemental analysis of the newly prepared material was sufficiently close to theory, however, to suggest strongly that at least a part of the contamination was due to decomposition during storage.

A solution of the impure 1,2-bis(difluoramino)ethane was chromatographed on a preparative scale with automatic injection, and the fraction indicated as peak A in Figure 11 was collected. A repress of the collected material gave the single peak shown in Figure 12.

F. SYNTHESIS AND PURIFICATION OF 1,1-BIS(DIFLUORAMINO)HEPTANE

A sample of the title compound, containing 1-1.5% heptanal, was prepared previously (Ref 2) for thermochemical studies. The purity was found to be inadequate for this purpose and purification by preparative v.p.c. did not appear to be feasible. We have since confirmed the finding that columns sufficiently polar to effect a separation cause decomposition of the gem-bis(difluoramino).

The synthesis of this compound was repeated using the procedure already reported (Ref 2). The crude product was treated with concentrated sulfuric acid, in the same manner described in paragraph D above. The final product had an infrared absorption spectrum (Ref 1) which demonstrated the absence of any water or carbonyl function, and an elemental analysis which indicated purity of the order of 99.9%.

Anal. calcd. for $C_7H_{14}N_2F_4$: C, 41.58; H, 6.98; N, 13.85; F, 37.59
Found: C, 41.36; H, 7.25; N, 14.04; F, 37.45

CONFIDENTIAL

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

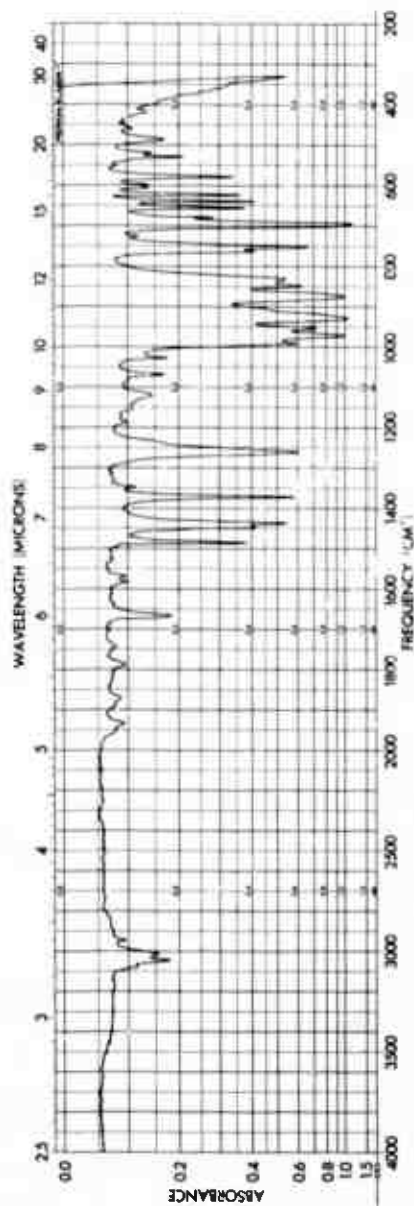


Figure 10. Infrared Spectrum of 1,1-Bis(difluoramino)phenylethane

CONFIDENTIAL

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

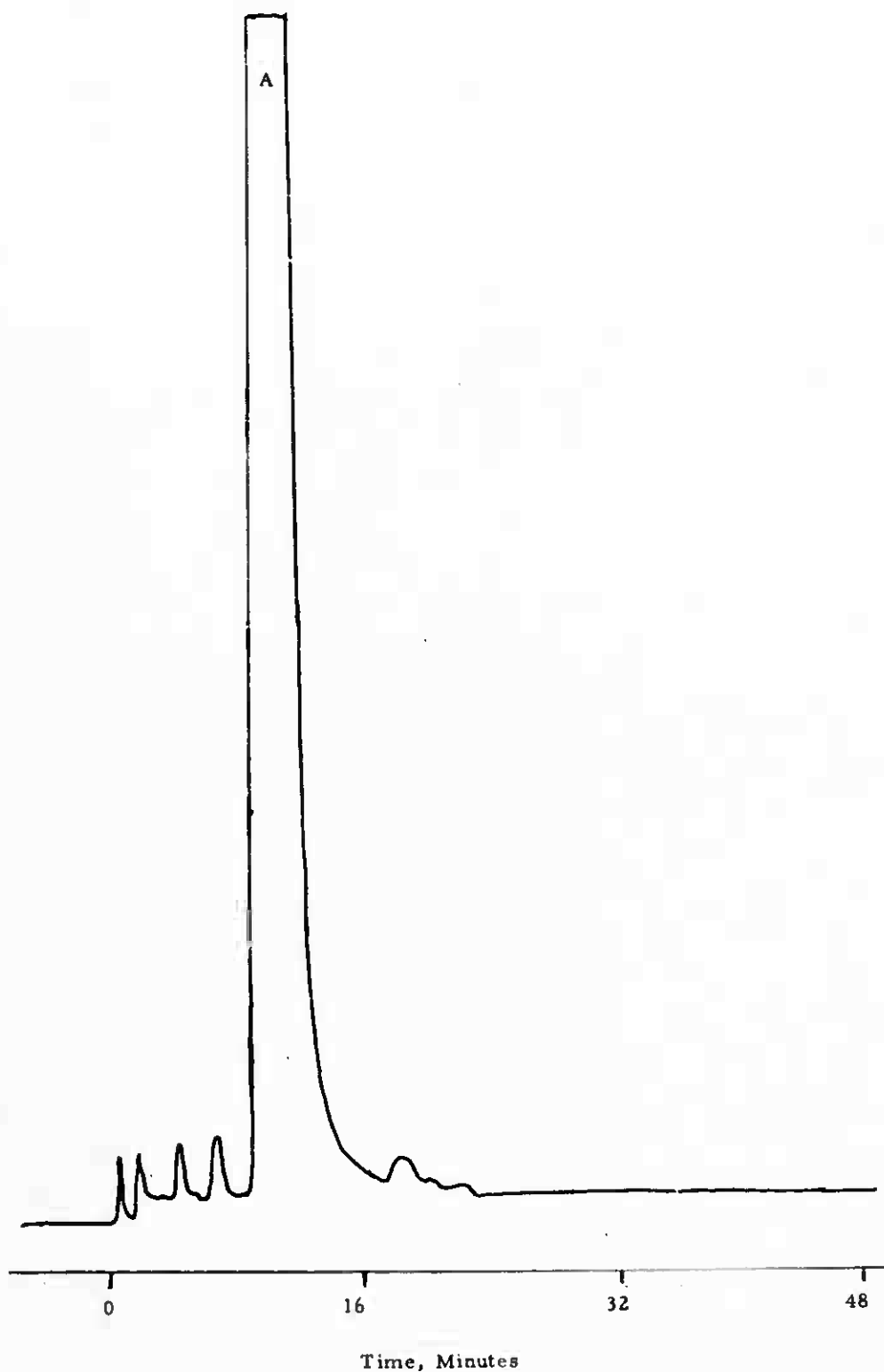


Figure 11. V.P.C. of 1, 1-Bis(difluoramino)ethane After 22 Months Storage

— 20 —

CONFIDENTIAL

Task 51
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

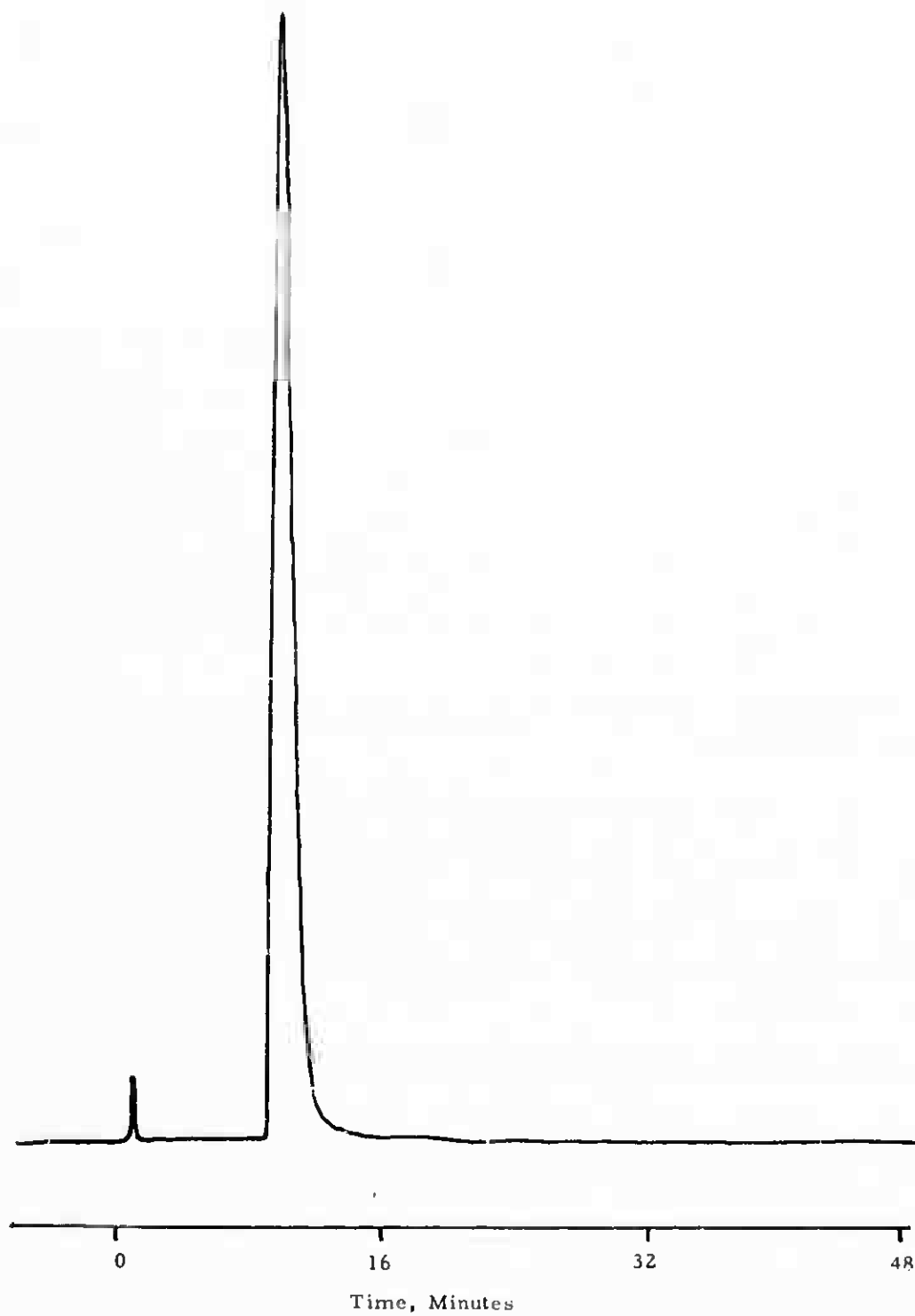


Figure 12. V.P.C. of Chromatographed 1,1-Bis(difluoramino)ethane

— 21 —

CONFIDENTIAL

Task 51
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

III. EXPERIMENTAL

A. 1-DIFLUORAMINO-2-FLUORIMINOCYCLOHEXANE

To 13.0 g. (0.0488 mole) of Amberlite IR-45 resin in 100 ml. CH_2Cl_2 was added dropwise 6.0 g. (0.0322 mole) of 1,2-bis(difluoramino)cyclohexane in 50 ml. CH_2Cl_2 . The reaction mixture was refluxed for 6 hr., cooled and filtered. The filtrate was then evaporated to yield 4.3 g. of a crude liquid. Distillation of the crude product yielded 3 fractions: 2.99 g. boiling at $40-46^\circ/3$ mm., 0.50 boiling at $48-50^\circ/3$ mm., and 0.36 g. boiling at $54-56^\circ/0.5$ mm. The first and third fraction were characterized by their infrared spectra as 1,2-bis(difluoramino)cyclohexane and 1,2-difluoriminocyclohexane, respectively. The middle fraction had an infrared spectrum which showed absorptions attributable to both $-\text{NF}_2$ and $=\text{NF}$ groups, possibly in the same molecule.

B. ATTEMPTED REACTION OF N, N, N'-TRIFLUOROBENZAMIDINE WITH n-BUTANOL

To a mixture of 0.1 g. of urea and 0.16 g. (0.0021 mole) of n-butanol in 5 ml. of Freon-113 at 0° was added dropwise a solution of 0.34 g. (0.0021 mole) of N, N, N'-trifluorobenzamidine. After the reaction mixture was stirred for 2 hr. at 0° , it was allowed to warm to ambient temperature and stirred overnight. The reaction mixture was then filtered and the filtrate evaporated to yield a crude liquid which consisted of n-butanol and the starting formamidine.

C. BIS(DIFLUORAMINO)FLUORAMINOMETHOXPENTANE

A mixture of 20 ml. Freon-113, 2.7 g. (0.031 mole) pentanol (Matheson Coleman and Bell), and 0.3 g. urea was placed in a Fisher-Porter reaction tube and degassed three times. The reactor was cooled to -120° and 1.12 l. of perfluoroguanidine measured at NTP (0.05 mole) was condensed in. After being allowed to warm up to 0° , the reactor was immersed in an ice bath and allowed to warm to 25° during 16 hr., with constant stirring. The remaining gas was then removed at 0° , and the reaction mixture was diluted with methylene chloride. The solution was stripped to yield 5.85 g. (86%) of crude product.

CONFIDENTIAL

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

A v.p.c. of the crude product on Halocarbon oil gave a curve with 3 peaks of approximately equal areas. For this reason, and despite the fact that no break appeared in the boiling point ($38-39^{\circ}/5.0$ mm.), the distillate was collected in 3 fractions. Each fraction gave a v.p.c. curve similar to that of the undistilled product. Material collected under the second peak was re-passed without change. The v.p.c. fraction represented by the third peak was converted on the column to a stable product having the same retention time as the original second peak.

D. 1,1-BIS(DIFLUORAMINE)PHENYLETHANE

To an aqueous solution containing 0.5 mole of difluorourea was added sulfuric acid. The liberated difluorourea was collected under Dry Ice reflux in a flask containing 7.0 ml. fuming sulfuric acid (104%). To this was added dropwise a solution of 6.17 g. (0.05 mole) of acetophenone in 20 ml. Freon-113. After the addition was complete, the mixture was stirred for an additional 0.5 hr. and the organic layer was separated, washed with water and aqueous bicarbonate and stripped of solvent. The crude product (2.8 g., 24% yield) was combined with that from several similar runs and distilled, b.p. $34^{\circ}/0.06$ mm.

E. 1,1-BIS(DIFLUORAMINO)HEPTANE

The difluoramine liberated from 1.0 mole of difluorourea was collected under Dry Ice reflux in a flask containing 7.0 ml. of 104% sulfuric acid. To this was added dropwise a solution of 5.10 g. (0.045 mole) heptanol (K and K Laboratory) in 10 ml. Freon-113. After 0.5 hr. of additional stirring, an additional 20 ml. of Freon-113 was added and the organic layer was separated.

To the combined products from two such runs was added 20 ml. 98% sulfuric acid, and the mixture was stirred vigorously for 20-30 min. The organic solution was then decanted off, washed with water and aqueous bicarbonate, dried, and stripped of solvent. The 8.0 g. of residue was distilled ($48^{\circ}/4.5$ mm.) to yield 5.5 g. of pure product.

CONFIDENTIAL

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

IV. FUTURE WORK

- One additional attempt to obtain a satisfactory yield of cyclohexyl-difluoramine, by the fluorination of ethyl N-cyclohexylcarbamate in acetonitrile solution, will be made.
- The conversion of bis(difluoramino)fluoraminomethoxypentane to the formamidine will be studied under a variety of conditions, with the intent of identifying the fragment eliminated.
- The N, N, N'-trifluoropentoxyformamidine obtained in these experiments will be utilized as a model compound for reaction studies.

CONFIDENTIAL

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

V. REFERENCES

1. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-Q2-65, Advanced Oxidizer Research (U), Section I, "Organic Difluoramine Chemistry", 30 June 1965
2. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-64-F, Advanced Oxidizer Research (U), Section I, "Difluoramine Chemistry", 31 December 1964
3. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-64-F, Advanced Oxidizer Research (U), "Synthesis of Compounds for Structure-Sensitivity Study", 31 December 1964
4. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-Q1-65, Advanced Oxidizer Research (U), Section I, "Organic Difluoramine Chemistry", 31 March 1965.
5. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD AOR-ATS-63, Advanced Oxidizer Research (U), Section II, "Synthesis of Compounds for Structure-Sensitivity Study", February 1964.

CONFIDENTIAL

SECTION II

TASK 53

INORGANIC OXIDIZER SYNTHESIS

Section II

Inorganic Oxidizer Synthesis

A. R. Young, II
S. I. Morrow

Report RMD 5043-Q3-65

RMD Project 5043, Task 53
Report Period: 1 July 1965 to
30 September 1965

Contract NONr 4364(00)
ARPA Order No. 417
Project Code 5910

FOREWORD

This section of the report summarizes the results of the synthesis of new inorganic oxidizers during the period from 1 July 1965 to 30 September 1965. This program was monitored by Mr. R. L. Hanson of the Office of Naval Research.

Personnel contributing to these studies were: A. R. Young (Project Supervisor), D. Moy and S. I. Morrow (Principal Investigators) and D. Kates, B. Fagan, and R. Crooker (Analytical Support).

ABSTRACT

Elemental analyses of the N_2F_4 - AsF_5 adduct give a composition, $N_2F_4(AsF_5)_{1.33}$, indicating a mixture of adducts having 1:1 and 1:2 $N_2F_4:AsF_5$ ratios. Evidence presented previously that the adduct is ionic and contains the $N_2F_3^+$ cation still appears valid. The structure of the 1:2 adduct is possibly $N_2F_3^+As_2F_{11}^-$.

The reaction of N_2F_4 with $HAsF_6$ gives a solid N-F compound having X-ray and infrared spectra different than $N_2F_3AsF_6$. No reaction occurred when N_2F_4 was treated with $HClO_4$ in HF. Unsuccessful attempts were made to prepare $N_2F_3ClO_4$ by reacting $N_2F_3AsF_6$ with metal perchlorates in HF.

The reaction of O_2AsF_6 with $CsClF_4$ produces O_2 and Cl_2 , as well as $CsAsF_6$, at about $0^\circ C$. The reaction of NO_2 with AsF_5 does not give a molecular adduct $NO_2 \cdot AsF_5$ as reported in the literature, but rather a mixture of $NOAsF_6$ and NO_2AsF_6 .

CONTENTS

	Page
I. INTRODUCTION	1
II. DISCUSSION	2
A. Inorganic N-F Chemistry	2
B. Dioxygenyl Salt Chemistry	12
III. EXPERIMENTAL	15
A. Reaction of N_2F_4 with $HAsF_6$	15
B. Attempted Reaction of N_2F_4 with $HClO_4$ in HF	15
C. Reaction of $N_2F_4(AsF_5)_x$ with $KClO_4$ in HF	16
D. Attempted Reaction of $N_2F_4(AsF_5)_x$ with $AgClO_4$ in HF	17
E. Reaction of N_2FAsF_6 with $CsClF_4$	18
F. Reaction of O_2AsF_6 with $CsClF_4$	18
G. Reaction of NO_2 with AsF_5	19
IV. REFERENCES	20

ILLUSTRATIONS

Figure		Page
1	Infrared Spectrum of $N_2F_4(AsF_5)_x$ Powder on AgCl	6
2	Infrared Spectrum of the Reaction Product of N_2F_4 with $HAsF_6$ (Powder Technique)	11

TABLES

I	Elemental Analysis of $N_2F_4(AsF_5)_x$	3
II	Emission Spectrum of N_2F_4 - $HAsF_6$ Product	9
III	Elemental Analysis of N_2F_4 - $HAsF_6$ Product	9
IV	X-Ray Pattern of N_2F_4 - $HAsF_6$ Product	10

I. INTRODUCTION

The concern of this portion of the Advanced Oxidizer Program is the study of the reactions of inorganic N-F and O-F compounds, the ultimate objective being the synthesis of new inorganic oxidizers. In previous work, we have shown that reactions of O_2F_2 and N_2F_2 in some cases yield ionic products containing the dioxygenyl (O_2^+) and fluorodiazonium (N_2F^+) ions, respectively. More recently, we have been studying adducts obtained by the reaction of N_2F_4 with AsF_5 which we believe to contain a new N-F cation, $N_2F_3^+$.

II. DISCUSSION

A. INORGANIC N-F CHEMISTRY

During the past quarter we continued our studies of adducts obtained by the reaction of N_2F_4 with AsF_5 . We have interpreted oreviously reported analytical, infrared, and F^{19} n.m.r. data (Ref 1 and 2) to be in support of the formulation of the adduct isolable at room temperature as $N_2F_3^+ AsF_6^-$. Our most recent analysis of this product, however, is not in agreement with the elemental composition required by this formula. Indeed, our present analytical data suggest that the adduct is a mixture of compounds of compositions $N_2F_4 \cdot AsF_5$ and $N_2F_4 \cdot 2AsF_5$. In spite of this unexpected result, the evidence presented previously in support of the existence of $N_2F_3^+$ in the adduct still appears to be valid.

In addition to further analytical studies of $N_2F_4(AsF_5)_x$, we examined reactions of N_2F_4 with $H_2F^+AsF_6^-$ (AsF_5 dissolved in HF), of N_2F_4 with $HClO_4$ in HF, and of $N_2F_4(AsF_5)_x$ with metal perchlorates in HF. The reactions of N_2F_4 with $H_2F^+ AsF_6^-$ and of $N_2F_4(AsF_5)_x$ with $AgClO_4$ gave results which indicate that further study of these systems is warranted.

• CHARACTERIZATION OF $N_2F_4(AsF_5)_x$

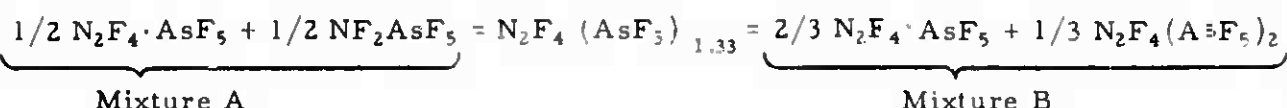
1. Stoichiometry

Previous data (Ref 1 and 2) giving the quantities of reagents consumed at $-80^\circ C$ in runs with varying initial quantities of N_2F_4 and AsF_5 yielded an average composition of $N_2F_4(AsF_5)_{2.3 \pm 0.2}$ for the low temperature adduct. When the adduct is allowed to warm to room temperature, additional AsF_5 is recovered and determinations of the net reagents consumed yield an average composition of $N_2F_4(AsF_5)_{1.2 \pm 0.2}$ for the room temperature adduct. During this quarter, a sample of the adduct was pumped at ambient temperatures for three days in the hopes of removing the last traces of AsF_5 , HF, and other volatile impurities. Independent

TABLE I
ELEMENTAL ANALYSIS OF $N_2F_4 \cdot (AsF_5)_x$

Element	Calcd. for $N_2F_4 \cdot AsF_5$	Calcd. for $N_2F_4 (AsF_5)_2$	Calcd. for $N_2F_4 \cdot (AsF_5)_{1.33}$	Found
F	62.42	59.93	61.31	62.15
N	10.23	6.31	8.37	8.39
As	27.35	33.76	30.22	30.56
Totals	100.00	100.00	100.00	101.10

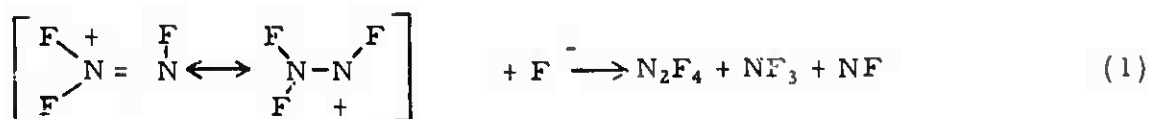
analyses for arsenic, nitrogen, and fluorine were run on this sample. The results obtained indicate a composition $N_2F_4 (AsF_5)_{1.33}$ (see Table I). It appears, then, that the non-integral AsF_5/N_2F_4 molar ratios calculated previously are not due to the presence of physically adsorbed arsenic pentafluoride, but are more likely due to the presence of a mixture of adducts having different AsF_5/N_2F_4 molar ratios, as shown below, namely:



Since the room temperature adduct apparently is a mixture of compounds (assuming that our elemental analyses prove to be reproducible), we must consider whether the strength of our previous arguments (Ref 1) that the adduct contains the $N_2F_3^+$ cation is diminished. These arguments are based on the following results, namely:

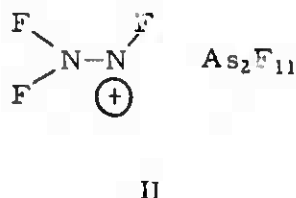
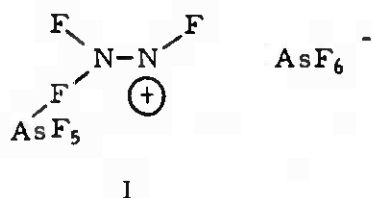
- Material balance measurements gave a value of 1.2 for AsF_5/N_2F_4 in the room temperature adduct. It was assumed that more precise analytical procedures would indicate a value of 1.0.
- The reaction of NaF with $N_2F_4 (AsF_5)_x$ liberated substantial quantities of NF_3 and N_2F_2 in addition to N_2F_4 , which would be the only product expected if the adduct were molecular and of composition $AsF_5/N_2F_4 = 1.0$.
- The F^{19} n.m.r. of $N_2F_4 (AsF_5)_x$ showed three non-equivalent fluorine on nitrogen peaks of equal intensity.

We believe that the observation of NF_3 and N_2F_2 as products of the reaction of NaF with $\text{N}_2\text{F}_4 \cdot (\text{AsF}_5)_x$ still provides strong support for the presence of a new ionic species, such as N_2F_3^+ , in the adduct. Even if $\text{N}_2\text{F}_4 \cdot (\text{AsF}_5)_x$ were a mixture of molecular adducts such as $\text{N}_2\text{F}_4 \cdot \text{AsF}_5$, NF_2AsF_5 , and $\text{N}_2\text{F}_4 \cdot 2 \text{AsF}_5$, we believe that N_2F_4 would be the sole gas liberated upon reaction with NaF . As shown previously (Ref 1), the presence of N_2F_2 and NF_3 in the products of the NaF reaction can be easily rationalized if one assumes an ionic constitution for $\text{N}_2\text{F}_3 \cdot (\text{AsF}_5)_x$ in which the cation is N_2F_3^+ (Equation 1).



Similarly, the argument for the presence of N_2F_3^+ based on the F^{19} n.m.r. spectra still appears to be valid. An ion such as N_2F_3^+ , having restricted rotation about the N-N Bond, would produce (as was observed) a spectrum showing three non-equivalent fluorine atoms of equal intensity. On the other hand, although there would indeed be three groups of non-equivalent fluorine atoms in a mixture of molecular adducts such as $\text{N}_2\text{F}_4 \cdot \text{AsF}_5$ and NF_2AsF_5 , it is doubtful that one could observe an n.m.r. signal in such a system, since NF_2AsF_5 would be paramagnetic. The other possible molecular mixture ($\text{N}_2\text{F}_4 \cdot \text{AsF}_5 + \text{N}_2\text{F}_4 \cdot 2\text{AsF}_5$) would, at the most, have only two groups of non-equivalent N-F fluorine atoms.

Thus, we can still feel fairly confident that the $\text{N}_2\text{F}_4 - \text{AsF}_5$ product is an ionic adduct containing the N_2F_3^+ ion. The non-integral values obtained for $\text{AsF}_5/\text{N}_2\text{F}_4$ ratio in the adduct in our analyses might be explained by the presence of structures such as I and II in addition to pure $\text{N}_2\text{F}_3^+ \text{AsF}_6^-$. During the next quarter we shall attempt to establish the reliability of our



elemental analysis and, if possible, to isolate pure $\text{N}_2\text{F}_3^+ \text{AsF}_6^-$.

2. Infrared Spectrum of $N_2F_4(AsF_5)_x$

We have continued studies of the infrared spectra of $N_2F_4(AsF_5)_x$ because we have obtained varying results (Ref 1 and 2) depending upon the method used in the preparation of infrared samples. During this quarter, we obtained an exceptionally well-resolved spectrum on a sample prepared by pressing finely divided $N_2F_4(AsF_5)_x$ between AgCl windows (Figure 1). This spectrum is in agreement with previous spectra (Ref 1) obtained by this powder technique. In addition to a doublet at 500 cm^{-1} and the $(\nu_3) AsF_6^-$ absorption at 695 cm^{-1} , there are strong absorptions at 920 cm^{-1} , 1110 cm^{-1} , and 1295 cm^{-1} and weak bands at 820 cm^{-1} , 990 cm^{-1} , 1420 cm^{-1} , and 1500 cm^{-1} . Spectra obtained by the powder technique have been consistently more complex than a spectrum obtained on a film of $N_2F_4(AsF_5)_x$ which was prepared by allowing AsF_5 and N_2F_4 to react on a AgCl window at -80°C (Ref 2). The latter spectrum shows only four peaks, namely: 700 cm^{-1} (AsF_6^-), 830 cm^{-1} , 920 cm^{-1} , and 1100 cm^{-1} . No satisfactory explanation for the difference in spectra obtained by the two techniques can be given at present. It is possible, however, that in the case of the powder spectra impurities are introduced during the sampling process (reaction with moisture) giving rise to the higher frequency bands (1295 cm^{-1} , 1420 cm^{-1} , 1500 cm^{-1}). Or it may be that the complexity of the powder spectrum (Figure 1) is simply due to the fact that $N_2F_4(AsF_5)_x$ is a mixture of adducts. Additional efforts will be expended during the next quarter on the identification of the absorption bands observed in the spectrum of $N_2F_4(AsF_5)_x$. It is anticipated that these efforts will contribute significantly to our knowledge of the structure of the adduct.

• REACTIONS OF $N_2F_4(AsF_5)_x$ WITH METAL PERCHLORATES

Reactions of $N_2F_4(AsF_5)_x$ with $KClO_4$ and with $AgClO_4$ were attempted during this quarter. These reactions were conducted in an "H"-shaped Kel-F apparatus using HF as a solvent medium. In the reaction with $KClO_4$, equimolar quantities of the solid reagents were mixed and placed in one leg of the "H"-tube. Upon distilling HF on the solid mixture, a pale yellow solution formed but a portion of the solid remained undissolved. The solution was decanted to the second leg and all volatiles were removed from the tube, leaving white solid residues in both legs. Only trace amounts of gaseous reaction products were observed, including NF_3 , ClO_3F , ClO_2 , and N_2O . The solids in both legs gave essentially the same X-ray and infrared spectra. The X-ray pattern indicates the presence of $KAsF_6$ and $NOClO_4$. Similarly, the infrared spectrum (NaF pellet) shows an absorption at 2080 cm^{-1} which might be attributed to NO^+ . However, there were also

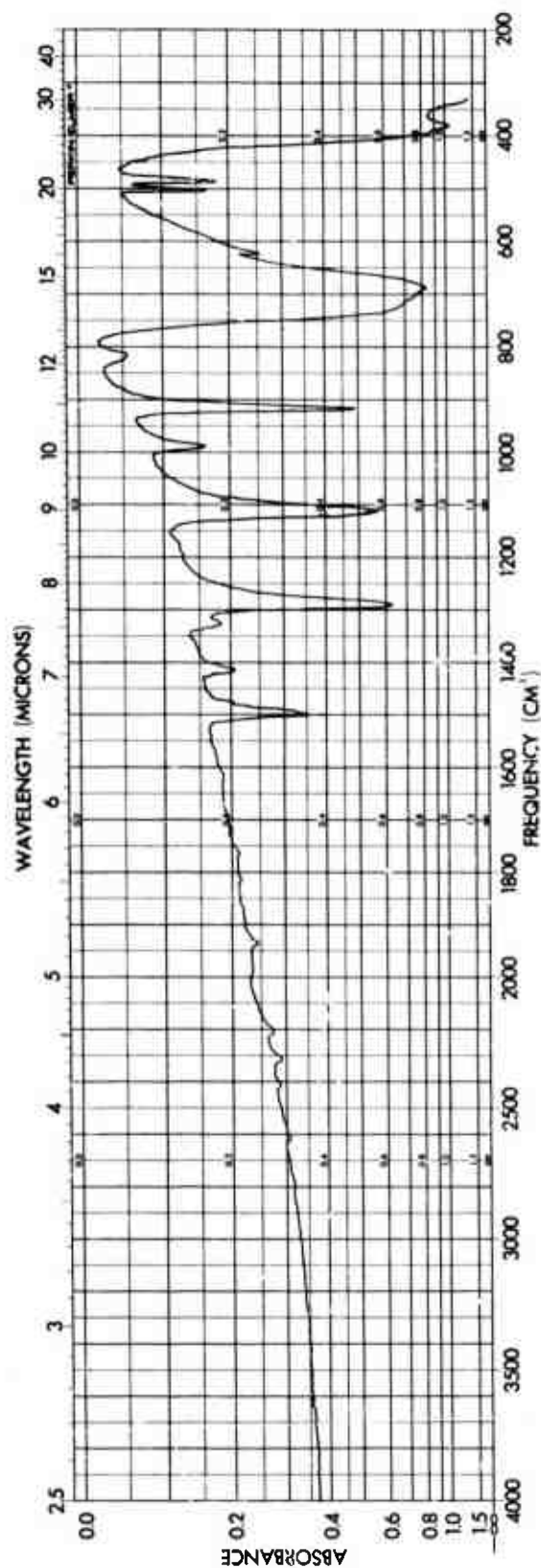


Figure 1. Infrared Spectrum of $N_2F_4(AsF_5)_x$ Powder on AgCl

absorptions at 930 cm^{-1} and 850 cm^{-1} which might be due to N-F. The strongest bands in the spectrum were at 1050 cm^{-1} (ClO_4^-) and 700 cm^{-1} (AsF_6^-). At this point, we are not certain whether NOClO_4 is an initial product of the reaction of $\text{N}_2\text{F}_4(\text{AsF}_5)_x$ with KClO_4 or whether it is obtained by the decomposition of an N-F perchlorate during the preparation of X-ray and infrared samples.

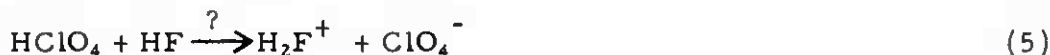
We made an attempt to investigate further the reaction of $\text{N}_2\text{F}_4(\text{AsF}_5)_x$ with ClO_4^- , using AgClO_4 as the source of the perchlorate ion. The change in perchlorate reagent was made because we expected to be better able to isolate a pure N-F perchlorate due to the insolubility of AgAsF_6 in HF (Equation 2).



However, we were unsuccessful in evaluating this reaction because the presence of an impurity (probably H_2O) in the HF caused the $\text{N}_2\text{F}_3\text{AsF}_6$ to decompose, liberating N_2O , NF_3 , and trans- N_2F_2 . Further studies of the reaction of $\text{N}_2\text{F}_4(\text{AsF}_5)_x$ with metal perchlorates in HF presently are being conducted.

• THE ATTEMPTED REACTION OF N_2F_4 WITH PERCHLORIC ACID IN HF

We recently attempted the preparation of $\text{N}_2\text{F}_3\text{AsF}_6$ by reacting N_2F_4 with a solution of AsF_5 in hydrogen fluoride. We obtained a solid product which we assumed to be $\text{N}_2\text{F}_3\text{AsF}_6$. Reasoning that the reaction proceeded as shown in Equations 3 and 4, we attempted to carry out an analogous reaction using the HClO_4 as the protonating agent shown in Equations 5 and 6.



N_2F_4 was condensed onto a solution of $HClO_4$ in HF and allowed to remain in contact with the solution for two weeks, after which the N_2F_4 was recovered virtually quantitatively. The failure of this reaction to proceed as predicted (Equations 5 and 6) led us to further investigate the solid we had obtained by the action of N_2F_4 on $HAsF_6$. As described in the next paragraphs, the solid proved to be an N-F compound, but of apparently completely different composition and structure than the adduct obtained by reacting N_2F_4 with AsF_5 in the absence of HF.

• THE REACTION OF N_2F_4 WITH $HAsF_6$

Since AsF_5 is such a strong acid (fluoride ion acceptor), it exists solely as AsF_6^- when dissolved in HF. It, therefore, occurred to us that if $N_2F_4(AsF_5)_x$ were a molecular addition compound no reaction should take place upon addition of N_2F_4 to a solution of $HAsF_6$ in HF. Molecular AsF_5 could only be made available in such a system by displacing the strong base F^- from AsF_6^- . If, on the other hand, a reaction did occur producing $N_2F_4-(AsF_5)_x$ this would be strong chemical evidence that this material is ionic (Equations 3 and 4).

When we allowed N_2F_4 to remain in contact with a solution of AsF_5 in HF for three days, we found upon stripping the solvent that a pale yellow solid product was obtained. The yellow color was due to the presence of a small amount of $Ni(AsF_6)_2$ (Ref 3) formed by the action of $HAsF_6$ on the Monel portions of the reactor. In spite of its yellow color, the solid appeared to be identical to the adduct obtained by reaction of N_2F_4 with AsF_5 in the absence of HF. For example, it reacted violently with water, producing oxides of nitrogen. However, as mentioned in the previous section, we decided to examine the solid more carefully to see if it were, indeed, identical to $N_2F_4(AsF_5)_x$. To our surprise, we obtained results from elemental analysis, infrared analysis, and X-ray analysis indicating that the product is different from the $N_2F_4-AsF_5$ adduct in both structure and composition. The data obtained are presented in Table II (emission spectrum), Table III (elemental analysis), Table IV (X-ray) and in Figure 2 (infrared spectrum).

TABLE II
EMISSION SPECTRUM OF N_2F_4 - $HAsF_6$ PRODUCT

<u>Element</u>	<u>Intensity</u>
As	High
Ni	Low
Cu	Trace
Mn	Trace
Fe	Faint Trace

Legend: High, more than 10%; Medium, 1 - 10%; Low, 0.1 - 1%
Trace, 0.01 - 0.1%

TABLE III
ELEMENTAL ANALYSIS OF N_2F_4 - $HAsF_6$ PRODUCT

<u>Element</u>	<u>Found</u>	<u>Calculated for $N_2F_4(AsF_5)_{1.33}$</u>
As	35.66	30.22
F	59.76	61.31
N	1.43	8.47
	<u>96.85</u>	<u>100.00</u>

TABLE IV

X-RAY PATTERN OF $N_2F_4-HAsF_6$ PRODUCT

$N_2F_4-HAsF_6$ Product		Principal Lines of $N_2F_4(AsF_5)_x$	
d, Å	I/I ₀	d, Å	I/I ₀
6.78	50	5.37	50
*5.73	3	4.45	100
5.26	10	3.38	100
*4.80	25	2.71	20
4.11	100	2.30	15
*3.98	10		
*3.51	50		
3.19	25		
*3.06	2		
*2.88	7		
2.75	4		
2.64	1		
2.57	4		
2.35	1		
2.25	2		
*2.16	8		
*1.77	10		
1.72	12		
1.57	4		
1.45	2		
1.38	8		
1.32	2		

* These lines also are present in the diffraction pattern of $Ni(AsF_6)_2$, according to a private communication from Dr. A. E. Pavlath of Stauffer Chemical Company, Richmond, Calif.

The infrared spectrum (Figure 2) is particularly interesting, for although it shows absorptions at 920 cm^{-1} , 1120 cm^{-1} , and 1295 cm^{-1} , similar to those found in $N_2F_4(AsF_5)_x$ (Figure 1), it does not show a single ν_3 absorption for AsF_6^- at 700 cm^{-1} . The absorption in the region of 700 cm^{-1}

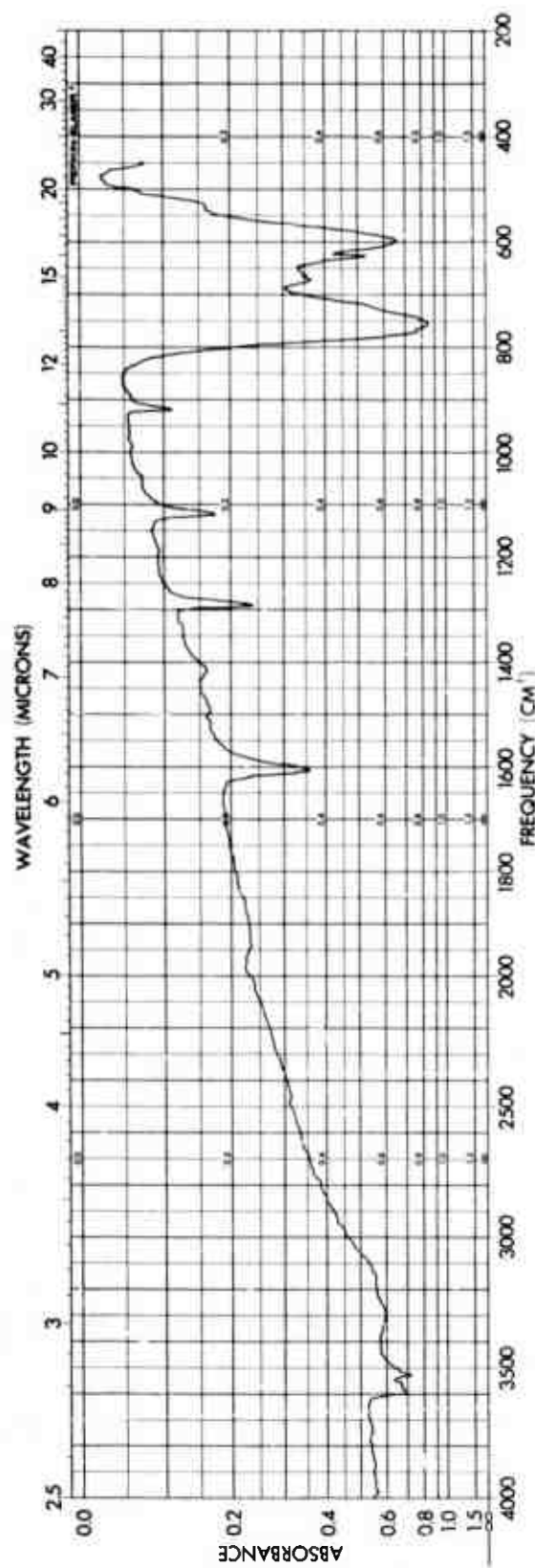


Figure 2. Infrared Spectrum of the Reaction Product of N_2F_4 with $HAsF_6$
(Powder Technique)

is split into four bands occurring at 755 cm^{-1} , 665 cm^{-1} , 630 cm^{-1} and 600 cm^{-1} . There is also a peak at 1600 cm^{-1} which does not appear in $\text{N}_2\text{F}_4(\text{AsF}_5)_x$. The complex band observed in the 700 cm^{-1} region of Figure 2 indicates considerable distortion of the AsF_6^- octahedra in this product. The nature of this distortion remains to be determined.

Even though our data show (Tables I and II) that elements other than N, As, and F were present in this product, we believe the data also show that the predominant component is a compound made up of these three elements, and that it is not the same as the adduct obtained from N_2F_4 and AsF_5 . We have constructed an all-plastic reactor (including a Teflon valve) for future runs involving the reaction of N_2F_4 with HAsF_6 in order to avoid contamination by metal hexafluoroarsenates. We hope to characterize the pure product during the next quarter.

• ATTEMPTED REACTION OF $\text{N}_2\text{F}^+\text{AsF}_6^-$ WITH CsClF_4

The preparation of N_2FClF_4 was attempted this quarter via a solid state reaction of N_2FAsF_6 with CsClF_4 (Equation 7). CsClF_4 (0.74 mmole) and N_2FAsF_6 (0.68 mmole) were mixed in a Kel-F tube at -78°C in vacuo. The



apparatus was attached to a mass spectrometer and the gases evolved were monitored at -78°C , -55°C , and 0°C . There was no appreciable gas evolution until the reactor reached 0°C , whereupon considerable pressure developed. The gases observed in the mass spectrometer were N_2O , N_2 , and O_2 , indicating that a leak had occurred in the system. Further attempts to determine whether N_2F^+ and ClF_4^- are compatible will be made during the next quarter.

B. DIOXYGENYL SALT CHEMISTRY

We have previously investigated the reaction of O_2AsF_6 and NO_2ClO_4 in the hope of preparing O_2ClO_4 (Ref 1 and 5) and concluded that the principal reaction occurring in this system was the formation of oxides of chlorine (most probably Cl_2O_6), NO_2AsF_6 , and possibly $\text{NO}_2\cdot\text{AsF}_5$. We have now determined that the reported preparation of $\text{NO}_2\cdot\text{AsF}_5$ (Ref 5) was probably erroneous since reactions of NO_2 with AsF_5 in various initial ratios yield a mixture of ionic adducts, NOAsF_6 and NO_2AsF_6 . We have also continued the study of the O_2AsF_6 - CsClF_4 reaction (Ref 2) during the current report period.

• REACTION OF O_2AsF_6 WITH $CsClF_4$

We continued to study the reaction of O_2AsF_6 with $CsClF_4$ because of the favorable ΔH_f value of -21 kcal/mole (Ref 2) calculated for the hypothetical salt, O_2ClF_4 . The desired reaction is:



Two experiments were carried out in which O_2AsF_6 and $CsClF_4$ were mixed together in a Kel-F reactor for several hours in a vacuum. In the first experiment, the amount of gases evolved during the reaction (O_2 , Cl_2 , and possible F_2) was only about half as great as expected if all of the O_2AsF_6 had been converted to O_2ClF_4 , i. e.:

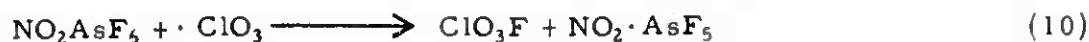


Despite this encouraging result, indicating that some O_2ClF_4 might have been left in the solid residue, hydrolyses of the solid residue failed to produce any oxygen. Dioxygenyl salts, such as O_2ClF_4 , produce oxygen and ozone under these conditions. X-ray analysis of the solid product showed that it was a mixture of $CsAsF_6$ and unreacted $CsClF_4$.

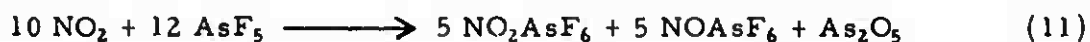
In the second experiment, an effort was made to determine whether there was an unstable intermediate formed in this reaction. The reactants were stirred in vacuo at -78° , whereupon traces of Cl_2 and O_2 in a ratio of 3:1 were evolved. Gas evolution upon standing overnight was negligible. The mixture was then stirred at 0° . A mixture of O_2 and Cl_2 in a ratio of 1.6:1.0 was evolved. The amount of gases evolved again was only about a third of that expected if O_2ClF_4 had been formed and then decomposed. However, X-ray analyses of the solid product gave only the diffraction pattern of $CsAsF_6$. It is difficult to get a clear picture of events in this system due to the fact that expected decomposition products of O_2ClF_4 , ClF , ClF_3 , and F_2 cannot be distinguished by the mass spectrometer. However, it does appear that O_2ClF_4 (if it forms) is unstable and decomposes at $0^\circ C$ or below.

• REACTION OF NO_2 WITH AsF_5

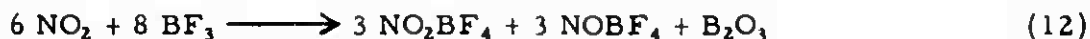
Prior work on the reaction of NO_2ClO_4 and O_2AsF_6 led us to suspect that the molecular adduct, $NO_2 \cdot AsF_5$, might have been a component of the solid products, in addition to NO_2AsF_6 . We postulated that the following reaction might have taken place (ClO_3F was one of the reaction products):



This suggested the presence of $\text{NO}_2 \cdot \text{AsF}_5$, which has been reported by Aynsley et al. (Ref 5), and might account for unknown X-ray lines in the product. When we originally tried to prepare $\text{NO}_2 \cdot \text{AsF}_5$ (Ref 2) by allowing NO_2 and AsF_5 to react in a vacuum, NOAsF_6 was obtained instead. We have explored this reaction further under varied conditions in the hope of obtaining $\text{NO}_2 \cdot \text{AsF}_5$. In every run we obtained a product which was predominantly NOAsF_6 , containing varying amounts of NO_2AsF_6 . We, therefore, feel that the reported existence of a molecular adduct, $\text{NO}_2 \cdot \text{AsF}_5$, is erroneous (Ref 5). The X-ray powder patterns of the products contained only one significant line at 3.85 \AA that could not be attributed to either NOAsF_6 or NO_2AsF_6 . The infrared spectra showed the ν_3 absorption of AsF_6^- at 700 cm^{-1} and absorptions in the $2200\text{-}2400 \text{ cm}^{-1}$ region where NO^+ and NO_2^+ have been reported to absorb (Ref 6). We postulate the following reaction (Equation 11) to account for the observed reaction products of the $\text{NO}_2\text{-AsF}_5$ reaction:



This reaction is analogous to one reported for the $\text{NO}_2\text{-BF}_3$ reaction (Ref 6, Equation).



III. EXPERIMENTAL

A. REACTION OF N_2F_4 WITH $HAsF_6$

Approximately 25 ml of hydrogen fluoride was treated with $N_2F_4(AsF_5)_x$ in order to remove last traces of water and other reactive impurities. The HF was then distilled to a Kel-F test tube fitted with a Monel valve and cooled to $-196^\circ C$. Roughly 4 mmoles of arsenic pentafluoride were condensed on the frozen HF, the valve was shut off and the tube was allowed to warm to room temperature in order to form a dilute solution of $HAsF_6$ in HF. The tube was recooled to $-196^\circ C$ and approximately 1 millimole N_2F_4 was condensed in it. The valve was closed and the tube was warmed to $-80^\circ C$, and a clear solution was observed. Over a period of several hours at $-80^\circ C$, a white precipitate formed in the tube. This was assumed to be $N_2F_3AsF_6$.

Three days later, after the tube had been standing at ambient temperature, it was decided to examine the solid product (completely dissolved at room temperature) more thoroughly. The HF was distilled to a receiver cooled to $-196^\circ C$ leaving a yellow solid residue in the reaction tube. This was pumped for several hours and then removed from the tube under dry N_2 for analysis. The yellow solid was quite reactive with water, producing flames and brown fumes (NO_2). Samples were examined by means of emission spectroscopy, elemental analysis, X-ray spectroscopy and infrared spectroscopy (Discussion Section, Tables II, III, and IV, and Figure 2). The results of these analyses showed that the solid contained metal hexafluoroarsenate impurities (predominantly $Ni(AsF_6)_2$) and that, although it was an N-F compound, it was not identical to the adduct obtained by the reaction of N_2F_4 with AsF_5 .

B. ATTEMPTED REACTION OF N_2F_4 WITH $HClO_4$ IN HF

Approximately 5 ml of anhydrous HF was dried over $N_2F_4(AsF_5)_x$ and distilled to a Kel-F tube fitted with a Monel valve. Four mmoles of anhydrous $HClO_4$ (prepared by dropping 70% $HClO_4$ into concentrated H_2SO_4) were condensed into the tube containing the HF at $-196^\circ C$. The tube was

warmed to room temperature in order to form a solution of HAsF_6 in HF . The tube was then re-cooled to -196°C and 0.5 mmole N_2F_4 was condensed into it. The system was then warmed to -80°C and maintained so for 10 days. The tube was then opened up to a vacuum line and pumped through two Kel-F traps at -80°C and -196°C , respectively. Roughly 0.5 mmole of unreacted N_2F_4 collected in the -196°C trap.

C. REACTION OF $\text{N}_2\text{F}_4(\text{AsF}_5)_x$ WITH KClO_4 IN HF

A 0.365 gms sample of an approximately 1:1 N_2F_4 - AsF_5 adduct (1.34 mmoles) was mixed with 0.200 gm KClO_4 (1.44 mmoles) in one leg of an "H"-shaped Kel-F reactor. The reactor was evacuated through a Monel valve and ball joint assembly, and 5 ml anhydrous HF was distilled onto the solid mixture at -196°C . The system was warmed to -78°C and agitated for two hr. During this period, a significant amount of solid remained undissolved in the HF but the HF solution became yellow. The tube was allowed to stand at -78°C for two days, and then volatile materials were removed by distilling from the reactor at -78°C to a trap at -196°C .

The material collected in the -196°C was predominantly HF . However, about 10%, or 0.2 mmoles, was shown by infrared to be a mixture of NF_3 , ClO_3F , ClO_2 , and N_2O . A portion of the yellow solution was then decanted to the second leg of the "H"-tube and the HF was completely distilled from the reactor. The solid residue from the yellow solution was white and showed the following infrared absorption (obtained on a sample pressed between AgCl plates):

1230	w. sharp	
1150-1030	s. broad	ClO_4^-
980	w. sharp	
855	w. sharp	
700	s. sharp	AsF_6^-
630	w. sharp	ClO_4^-

In order to obtain a better spectrum, a sample was mixed with dry NaF and a pellet was pressed. This exhibited the following absorptions:

2090 cm^{-1}	$(\text{NO}^+?)$
1050 cm^{-1}	ClO_4^-
930 cm^{-1}	
850 cm^{-1}	
700 cm^{-1}	AsF_6^-

The X-ray diffraction pattern of solid isolated from the HF solution was as follows:

$d, \text{\AA}$	I/I_0	KAsF ₆ (Ref 4) $d^{\circ}, \text{\AA}$
*5.64	10	---
4.83	90	4.82
*4.48	30	---
*3.91	15	---
3.70	100	3.68
*3.61	30	---
*3.54	30	---
*3.37	10	---
*3.19	90	3.16
*2.92	20	2.92
*2.87	30	---
*2.55	15	---
2.42	5	2.40
*2.30	3	2.29
*2.25	1	---
*2.17	20	---
2.15	10	2.12
2.03	70	2.00
*1.90	2	---
1.85	7	1.84

* Diffraction lines present in pattern of NOClO₄

An attempt was made to obtain nitrogen content of the solid by hydrolysis. A 90 mg sample was weighed into a dry glass (under N₂) tube fitted with a stopcock ball joint assembly. However, the solid immediately began to evolve NO₂. The tube was rapidly evacuated and water distilled onto the solid at -196°C. Upon warming to room temperature, the solid went into solution with vigorous gassing. The gas (4.5 mg) was nitric oxide.

D. ATTEMPTED REACTION OF N₂F₄(AsF₅)_x WITH AgClO₄ IN HF

A 0.255 gm of AgClO₄ and 0.284 gm of N₂F₄(AsF₅)_x were weighed into separate legs of the "II" reactor. The tube was evacuated and 5 ml of dry HF was distilled onto the N₂F₄(AsF₅)_x at -196°C. Upon warming the tube to room temperature, the N₂F₄(AsF₅)_x went into solution with vigorous gas evolution.

Approximately 1 mmole of a mixture of NF_3 , N_2F_2 , and N_2O was formed in the process. The experiment was discontinued because of the obvious decomposition of the adduct.

E. REACTION OF N_2FAsF_6 WITH CsClF_4

A 59.0 cc volume Kel-F, metal reactor with a small vacuum gauge attached to it was used in this experiment. A 0.18 gm sample of CsClF_4 was loaded into a swivel-side arm. The 0.16 gm of N_2FAsF_6 was placed in the bottom of the reactor along with a Teflon coated stirring bar. The CsClF_4 was dropped into the reactor under vacuum conditions at -78°C . No significant rise in pressure was noted when this was done, but traces of gases were detected by the mass spectrometer which had the following composition: Cl_2 65%, O_2 28%, CO_2 3%, and ClO_3F 4%. The reactor was held at -78° overnight. The next morning the pressure was ≤ 25 mm. These gases were pumped out and the reactor was warmed to -55° and held there for 1 hr. No gases were detected by the mass spectrometer. The reactor was then warmed to 0°C and within 5 minutes, during which the reagents were being stirred, the pressure rose to ≈ 250 mm. The composition of this gas as determined by mass spectroscopy was N_2O , N_2 , and O_2 . The ratio of $\text{N}_2:\text{O}_2$ was similar to that in air. No NF^+ or ClF^+ fragments were detected. These gases were removed and the reactor was allowed to stand several days in a vacuum at room temperature. A 0.34 mmole mixture of gas was then found in the reactor, which had the composition 50% O_2 , 15% N_2O , 35% N_2 . Again the presence of air was indicated.

The solid residue from the reaction is being analyzed.

F. REACTION OF O_2AsF_6 WITH CsClF_4

A 59.0 cc volume metal, Kel-F reactor with a vacuum gauge was used for this reaction. A 0.25 gm sample of CsClF_4 was loaded into the swivel-side arm and 0.22 gm of O_2AsF_6 was loaded into the bottom of the reactor along with a Teflon covered magnetic stirring bar. The reactants were mixed in vacuo at -78° , whereupon only a trace of gas was evolved. This was composed of Cl_2 and O_2 in the ratio of 3:1. The mixture was next stirred at 0°C . A 1.0 mmole quantity of gas was generated, which was composed of $\text{O}_2:\text{Cl}_2$ in a ratio of 1.6:1.0. A trace of ClO_3F was also detected. The solid product, which was a dark, fused mass, weighed 0.20 gm. Its X-ray powder pattern was in agreement with that of CsAsF_6 .

G. REACTION OF NO_2 WITH AsF_5

A typical experiment was carried out in a glass reactor which had a volume of about 150 cc. In this particular instance, 0.2139 gm of NO_2 was condensed into the lower half of the reactor at -196° . Then 0.7805 gm of AsF_5 reagent (58.2% AsF_5 , the rest BF_3 and SiF_4) was condensed onto the frozen NO_2 at -196° . The stoichiometric ratio of $\text{NO}_2:\text{AsF}_5$ was 1.75:1.00. The reactor was then placed in an unsilvered Dewar flask, and prechilled with liquid N_2 . The open part of the Dewar was packed with glass wool and the reactor was allowed to warm from -196° to room temperature. Due to the fact that the Dewar was prechilled, this took place slowly. Reaction was observed to take place vigorously at about 25°C . Both white and yellow solids formed in the reactor. The yellow material formed in the bottom. A 7.6 mg quantity of O_2 was evolved. This was removed while the reactor was kept at -78°C . When the reactor was warmed to -56° and held there for an hour, 36.8 mg of a mixture of NO_2 , SiF_4 , and traces of HNO_3 were removed. The reactor was warmed to room temperature. Nitrogen dioxide was evolved from the yellow solid as it turned white and began to crumble to a powder. The weight of gas evolved was 35.1 mg. Infrared analysis showed this was NO_2 with a trace of HNO_3 . The weight of the white solid left after removal of all of the gases was 0.8709 gm. This represented 149% of the weight of NOAsF_6 expected from the quantity of AsF_5 used. A sample of the adherent white solid was removed from the walls and analyzed by X-ray spectroscopy. It was a mixture of NOAsF_6 with lesser amounts of NO_2AsF_6 . A strong "d" line at 3.86 Å could not be identified with either; however, a sample of powdery white material from the bottom of the flask, which was a decomposition product of the yellow material, also was analyzed by X-ray. Its composition was the same as that from the walls. Some of the solid product was analyzed by infrared spectroscopy by smearing it onto AgCl plates. Bands were observed at: 2370 cm^{-1} (NO^+ or NO_2^+), 895, 695 (AsF_6^-), and 584 cm^{-1} .

IV. REFERENCES

1. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-Q1-65, Advanced Oxidizer Research, 31 March 1965 (C)
2. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-Q2-65, Advanced Oxidizer Research, 30 June 1965 (C)
3. Stauffer Chemical Company
4. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-64-F, Advanced Oxidizer Research, 14 December 1964 (C)
5. E. Aynsley, R. Peacock, P. Robinson, Chem. And Ind., 1117, 1951
6. J. C. Evans, et al., Inorg. Chem., 3, 857, 1964
7. R. B. Roof, Acta. Cryst., 8, 739, 1955

SECTION III

TASK 55

THERMAL STABILITY
OF ADVANCED SOLID OXIDIZERS

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

SECTION III

THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

C. J. Grelecki
W.J. Cruice

Report RMD 5043-Q3-65

RMD Project 5043, Task 55
Report Period: 1 July 1965
to 30 September 1965

Contract No. NONr 4364(00)
ARPA Order No. 417
Project Code 5910

CONFIDENTIAL

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

PREVIOUS PAGE WAS BLANK, THEREFORE NOT FILMED.

FOREWORD

This section of the advanced oxidizer report summarizes work carried out during the period from 1 July 1965 to 30 September 1965 on the thermal stability of advanced solid oxidizers (RMD Project 5043, Task 55).

Contributors to the research were: C. Grelecki (Project Supervisor) and W. Cruice (Principal Investigator).

— iii —

CONFIDENTIAL

Task 55
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

ABSTRACT

The presence of ammonium perchlorate as a decomposition product of hydroxylammonium perchlorate was found to be dependent on the removal of oxidizing species from the system and, hence, non-stoichiometric. The oxidation of ammonium perchlorate by anhydrous perchloric acid at elevated temperatures was demonstrated.

— iv —

CONFIDENTIAL

Task 55
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

CONTENTS

	Page
I. INTRODUCTION	1
II. SUMMARY	2
III. EXPERIMENTAL	
A. Procedures	3
B. Materials	3
IV. RESULTS AND DISCUSSION	
A. Stoichiometry Experiments	5
B. Ammonium Perchlorate — Perchloric Acid Systems	5
C. General Discussion	6
V. FUTURE WORK	8
VI. REFERENCES	9

— v —
CONFIDENTIAL

Task 55
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

I. INTRODUCTION

The objective of this program is to study the kinetics of the thermal reactions of high energy solid oxidizers in order to understand the mechanism by which they decompose. Work previously reported includes a detailed literature search, results of experimental work on the vapor pressure and thermal decomposition of anhydrous perchloric acid, determination of the temperature coefficients of the reactions of hydrazinium monoperoxchlorate, hydroxylammonium chloride, and hydroxylammonium peroxchlorate, determination of the reaction stoichiometry of hydrazinium monoperoxchlorate, studies on the reaction stoichiometry of hydroxylammonium peroxchlorate, and results of some preliminary experiments on hydrazinium diperoxchlorate.

Destructive distillation experiments have been performed on high purity hydroxylammonium peroxchlorate and the results compared with the results of closed-system experiments of the kind previously reported. Basic exploratory studies have been conducted to determine whether ammonium peroxchlorate can be oxidized by perchloric acid at temperatures comparable to those where hydroxylammonium peroxchlorate decomposes.

This report includes a summary of experimental work done in the third quarter of 1965 and a brief outline of projected work for the following quarter.

— 1 —

CONFIDENTIAL

Task 55
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

II. SUMMARY

During this report period, the thermal decomposition of hydroxyl-ammonium perchlorate was found to produce ammonium perchlorate only if the volatile products were constantly removed. The stoichiometry for decomposition of free hydroxylamine was found to be inapplicable, indicating definite oxidation of some intermediate which normally decomposes spontaneously to yield ammonia. The oxidation of ammonium perchlorate by anhydrous perchloric acid to yield nitrous oxide was demonstrated, although the normal decomposition of the acid is the preferred reaction. Additional experiments directed toward discovery of the stoichiometry and mechanism of the reaction are under way.

CONFIDENTIAL

Task 55
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

III. EXPERIMENTAL

A. PROCEDURES

1. Stoichiometry Experiments

The methods used in these experiments have been discussed in detail in Reference 1.

2. Ammonium Perchlorate — Perchloric Acid Systems

Thermal decomposition experiments were performed on mixtures of ammonium perchlorate and, alternately, perchloric acid dihydrate, hydroxylammonium perchlorate, and anhydrous perchloric acid. The additive was introduced into a preweighed Sickie gauge (Ref 2) containing a weighed amount of ammonium perchlorate. The gauge was set into liquid nitrogen, evacuated immediately, and sealed. The sealed gauge plus the fragment removed in sealing then were reweighed and the weight of additive determined. The balance of the experiment proceeded in the manner previously referenced.

B. MATERIALS

1. Hydroxylammonium Perchlorate

The production of hydroxylammonium perchlorate is detailed in Reference 1.

2. Anhydrous Perchloric Acid

The production of anhydrous perchloric acid is detailed in Reference 2.

3. Perchloric Acid

Baker 72% perchloric acid (ACS) was employed as perchloric acid dihydrate for the purposes of this experiment. The actual assay was 71.1% HClO_4 , corresponding to a 2.27 molar ratio of H_2O to HClO_4 .

CONFIDENTIAL

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

4. Ammonium Perchlorate

The ammonium perchlorate used in these experiments was Matheson, Coleman and Bell reagent grade, assayed at RMD at over 99% purity.

— 4 —

CONFIDENTIAL

Task 55
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

IV. RESULTS AND DISCUSSION

A. STOICHIOMETRY EXPERIMENTS

1. Destructive Distillation of Hydroxylammonium Perchlorate

Hydroxylammonium perchlorate was maintained at 180°C for periods of approximately 18 hr; the system was continually evacuated through a liquid nitrogen trap at a pressure of 0.05 mm Hg. The reactant initially melted and rapid gassing was observed. However, after a period of time, the sample was observed to congeal, forming a white solid. This solid residue accounted for 20% of the starting mass; it was composed of 42.5% hydroxylammonium perchlorate, 39.1% ammonium perchlorate and 18.0% perchloric acid dihydrate. The remaining 0.4% was assumed to be additional water.

If the stoichiometry



were to apply, however, the residue would account for at least 44% of the starting material, based on pure ammonium perchlorate. Therefore, the above stoichiometry cannot apply to this reaction without further reservations. The products isolated from the cold traps were found to be nitrous oxide, hydrogen chloride, and another strong acid. There was not enough of the latter to permit adequate identification, but it appears to have been perchloric acid.

B. AMMONIUM PERCHLORATE — PERCHLORIC ACID SYSTEMS

As previously stated (Ref 1), products of the decomposition of hydroxylammonium perchlorate in sealed systems are nitrous oxide, hydrogen chloride and chlorine in the vapor phase. The condensed residue is a colorless liquid which may solidify slightly above ambient temperature. No ammonia has been detected in this residue, and it was supposed that the ammonia predicted by the above stoichiometry might be oxidized by perchloric acid produced in the reaction.

CONFIDENTIAL

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

In order to verify this assumption, a number of thermal decomposition experiments were performed on ammonium perchlorate mixtures containing (alternately) hydroxylammonium perchlorate, perchloric acid dihydrate, and anhydrous perchloric acid. No decomposition was observed when a mixture of ammonium perchlorate and perchloric acid dihydrate was maintained at 150°C for an extended period.

An approximately equimolar mixture of ammonium perchlorate and hydroxylammonium perchlorate was maintained at 150°C for 150 minutes. Examination of the residue showed a slight increase in the total mass of ammonium perchlorate. Less hydroxylammonium perchlorate was consumed than would have been consumed in such an experiment performed on pure hydroxylammonium perchlorate.

Mixtures of ammonium perchlorate and anhydrous perchloric acid were run at 55°C, 70°C, and 100°C. At the lower temperatures, the molar ratios employed were (AP:HClO₄) 5:1 and 3:1 respectively, whereas at 100°C the molar ratio was approximately 1:2. At 55°C, normal decomposition products of anhydrous perchloric acid were obtained in the vapor phase, although the rate of pressure rise was lower than that observed for the pure acid. At 70°C, traces of N₂O were detected in the vapors and at 100°C (where the mixture decomposed instantaneously), 2% N₂O was detected. Thus, oxidation of the ammonia moiety of ammonium perchlorate by perchloric acid at elevated temperatures is definitely possible.

C. GENERAL DISCUSSION

The following specific facts concerning the thermal decomposition reaction of hydroxylammonium perchlorate are now fairly well established:

— The reaction in a closed system proceeds to nitrous oxide, hydrogen chloride and chlorine, and a strongly acidic liquid. No ammonium perchlorate is produced.

— The reaction in a constant vacuum proceeds to nitrous oxide, hydrogen chloride and chlorine, and a solid containing ammonium perchlorate, perchloric acid dihydrate and unreacted hydroxylammonium perchlorate. The amount of ammonium perchlorate produced does not correspond to the stoichiometry proposed for simple decomposition of free hydroxylamine.

CONFIDENTIAL

Task 55
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

— The kinetic data do not indicate competing reactions; the value of the activation energy indicates that the rate-controlling step in the early stages of the reaction is not the same as in hydrazinium mono- or diperchlorate or anhydrous perchloric acid. Likewise, it is not the same as in the decomposition of free hydroxylamine.

Thus it appears that the difference in end-product residue between the sealed system and the evacuated system is due to the removal of oxidizing species in the evacuated system. The reaction proceeds through some intermediate which may be oxidized to yield only nitrous oxide or may decompose spontaneously to yield nitrous oxide and ammonia. Such reactions should be first order with respect to oxidizing species and with respect to intermediate in the first case, and first order with respect to intermediate only in the second. Since the concentration of oxidants is high in the closed system but low in the evacuated system, the spontaneous decomposition should occur to a much higher degree in the evacuated system (as is the case). It appears that the rate constant for oxidation is greater than that for spontaneous decomposition, since no ammonia at all is found in the closed system.

— 7 —

CONFIDENTIAL

Task 55
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

V. FUTURE WORK

Additional work on the stoichiometry and mechanism of thermal decomposition of hydroxylammonium perchlorate is required. Specific objectives for the following report period include:

- Complete thermal decomposition of samples of hydroxylammonium perchlorate to obtain mass balance,
- Reexamination and integration of experimental results and information in the literature to propose a mechanism of decomposition.

CONFIDENTIAL

Task 55
Report RMD 5043-Q3-65

CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

VI. REFERENCES

1. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-Q2-65, Advanced Oxidizer Research, Section III, 30 June 1965 (C)
2. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-64-F, Advanced Oxidizer Research, Section IV, 14 December 1964 (C)

— 9 —

CONFIDENTIAL

Task 55
Report RMD 5043-Q3-65

Confidential

Security Classification

DOCUMENT CONTROL DATA - R&D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) Thiokol Chemical Corporation Reaction Motors Division Denville, New Jersey		2a. REPORT SECURITY CLASSIFICATION Confidential
		2b. GROUP Group IV
3. REPORT TITLE Advanced Oxidizer Research (U)		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Quarterly Progress		
5. AUTHOR(S) (Last name, first name, initial) Smith, H.F.; Dvorak, J.J.; Young, A.R.; Morrow, S.J.; Grelecki, C.J.; Cruice, W. J.		
6. REPORT DATE 30 September 1965	7a. TOTAL NO. OF PAGES 72	7b. NO. OF REFS 14
8a. CONTRACT OR GRANT NO. NONr 4364(00)	9a. ORIGINATOR'S REPORT NUMBER(S) RMD 5043-Q3-65	
b. PROJECT NO. ARPA Order No. 417, Amendment No. 2	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c. Tasks 51, 53, 55		
d. Code 0810		
10. AVAILABILITY/LIMITATION NOTICES		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Advanced Research Projects Agency (Office of Naval Research)	
13. ABSTRACT <p>Task 51 - Further experiments on the dehydrofluorination of secondary alkyl-difluoramines are described. A new partially dehydrofluorinated product, 1-difluoramino-2-fluoriminocyclohexane, was obtained by treating bis(difluoramino)cyclohexane with basic ion exchange resin for a limited time. Bis(difluoramino)fluoraminomethoxypentane was synthesized by the addition of pentanol to perfluoroguanidine.</p> <p>Task 53 - Elemental analyses of the $N_2F_4 \cdot AsF_5$ adduct gave a composition, $N_2F_4(AsF_5)_{1.33}$, indicating a mixture of adducts having 1:1 and 1:2 $N_2F_4 \cdot AsF_5$ ratios. The structure of the 1:2 adduct possibly is $N_2F_3^+ As_2F_{11}^-$. (U)</p> <p>The reaction of O_2AsF_6 with $CsClF_4$ produced O_2 and Cl_2, as well as $CsAsF_6$, at about $0^\circ C$. The reaction of NO_2 with AsF_5 does not give a molecular adduct $NO_2 \cdot AsF_5$ as reported in the literature, but rather a mixture of $NOAsF_6$ and NO_2AsF_6. (U)</p> <p>Task 55 - The presence of ammonium perchlorate as a decomposition product of hydroxylammonium perchlorate was found to be dependent on the removal of oxidizing species from the system and, hence, non-stoichiometric.</p>		

DD FORM 1 JAN 64 1473

Confidential

Security Classification

Confidential

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Dehydrofluorination Alkyldifluoramines Pentanol Perfluoroguanidine Adduct Ammonium Perchlorate Anhydrous Perchloric Acid Hydroxylammonium Perchlorate						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (corporate author) issuing the report.

2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (either by the originator or by the sponsor), also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (paying for) the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

Confidential

Security Classification